ANNUAL PROGRAM REVIEW

CORROSION CONTROL

March 13, 1998

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Institute of paper Science and Technology
500, 10th Street, NW
Atlanta, GA 30318

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RECOVERY BOILER CORROSION

ANNUAL RESEARCH REVIEW

March 13, 1998

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TECHNICAL PROGRAM REVIEW

Project Title:	RECOVERY BOILER CORROSION
Project Number:	F018
Division:	Chemical Recovery and Corrosion Division
Project Staff:	P. Singh, G. Fonder, S. Al-Hassan
FY 96-97 Budget:	$30,987

Program Objectives:
Improve safety and increase operating life of equipment by proper selection of construction materials, suitable process conditions, and by understanding the possible corrosion processes in kraft recovery boilers.

Project Summary:
This section describes projects related to recovery boiler corrosion, which are directly funded by the member dues, as well as other recovery boiler related projects on-going at IPST.

Main objective of the member-dues funded, project was to study the long-term corrosion kinetics of 1018 carbon steel in 1% H_2S at 400°C for up to 10,000 hours of exposure. Major concerns, which led us to do this experiment, were to study if the sulfide scale spalls during long exposure, and if the breakaway corrosion occurs for the carbon steel during 10,000 hour exposure. Weight changes are measured at relatively short intervals of time. Results from the 10,000 hour exposure test have shown that the corrosion reaction kinetics follows a classic sulfidation behavior where the initial corrosion rate is controlled by the reaction which is followed by the diffusion controlled reaction processes. There were no indications of the scale spalling during this test. Specimen and the corrosion products were examined using scanning electron microscopy (SEM) and analyzed using energy dispersive spectroscopy (EDS) after the completion of this test.

Task II of this project is related to the DOE/AF&PA project on corrosivity in kraft recovery boilers. Objective of this task is to develop a basic understanding of the smelt/gas interactions and their resultant effects on the corrosion of the waterwall tube surfaces from the fireside. Published results from various authors and previous tests done at IPST indicate that the presence of smelt can increase the corrosion rates in high temperature gaseous environments. Recovery boiler tubes, during operation, are covered with the frozen smelt whose composition may vary with time and position. Bulk gases have to diffuse through the smelt to the smelt/metal interface for the corrosion reactions to take place on the boiler tubes. Changes in gas composition due to the reactions of gas with smelt will affect the corrosion characteristics of the tube material. Therefore, we have setup an experimental program to generate these data and to increase our understanding of the effects of the smelt composition on the corrosion rate of water wall tube materials. Test setup was designed so that we could use our existing gaseous corrosion test apparatus. Results from these tests show that the corrosion rates of SA-210 carbon steel exposed to the 1% H_2S gas passed through the smelt can change considerably depending upon the initial composition of the smelt. We are in process of setting up an on-line gas chromatographic equipment which will be used to study the smelt/gas reactions. Capability to analyze gas composition changes will provide us with much required understanding of these interactions and also help in explaining the corrosion behavior of the materials exposed to the resultant environments.

Another project related to the composite tube cracking in the kraft recovery boilers was funded by Oak Ridge National Laboratory. Objectives of this project are to explore the possible stress corrosion cracking (SCC) mechanisms, which can operate during the shutdown conditions. Results of the ORNL investigation and other published results indicate that the composite tube cracking in kraft recovery boilers may be due to SCC. Various possible environments, including different constituents of washwater, are being studied in this project. SCC susceptibilities of different microstructures of stainless steel in the possible recovery boiler environments during the shut down condition will also be studied. Slow strain rate tests were carried out to screen the possible wash water compositions and other environmental variables, which are capable of causing stress corrosion cracking of stainless steel composite tubes. Results from this study have shown that typical washwaters are capable of causing stress corrosion cracking of 304L stainless steels at temperatures between 150°C & 200°C and above. We will be doing some slow strain rate tests with applied potential at lower temperatures to see if the cracking is possible in certain potential range at these temperatures. We hope that this systematic study will answer some of the present cracking problems as well as indicate other possible mechanisms of stress corrosion, which can possibly operate in the recovery boiler environments.

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Introduction

The main objective of the projects described in this section is to understand the causes of corrosion and stress corrosion cracking of the waterwall tubes in the lower furnace of the kraft recovery boiler. Better understanding of these causes is necessary to develop successful corrosion mitigation strategies. Different types of material-related problems on the fireside have been observed and reported by various mills, and corrosion has been implicated in several smelt-water explosions over the years. Obviously, safe operation of the boiler is of prime concern, so the objective of the research program at IPST is to develop a sound understanding of the general and specific corrosion problems of kraft recovery boilers.

The focus of this program is consistent with IPST's goals for its dues-funded research program in that it is aimed at long term implications with an emphasis on a fundamental understanding rather than a short-term quick fix without any understanding of the underlying reasons for the observed behavior. Parts of this program are leveraged with a large DOE/AF&PA project and a relatively smaller ORNL-funded project whose general objectives overlap with the overall objectives of this project.

Discussion of FY 96-97 Results

Research in the recovery boiler area, carried out at IPST in 1996-97, can be divided into two different tasks. Table 1 gives an overview of the structure of the overall research efforts in this area and shows how member dues-funded projects are leveraged with other externally funded projects and student research. Next to each task is a brief description of the main objective or the question that needs to be answered.

Table I. Recovery Boiler Related on-going Projects at IPST

Dues-Funded (F018)	***Additional Funding Leverage***
Task 1. Long-term Kinetics To understand long-term kinetic changes in sulfidation of carbon steels	
Task 2. Gas/Smelt Interactions and Their Effects on Corrosion of SA-210 alloy To generate basic understanding of smelt/gas interactions and their effects on the corrosion processes in lower furnace environments	DOE/AF&PA Corrosivity Monitoring of Kraft Recovery Boilers
Externally Funded Projects	
Corrosivity Monitoring of Kraft Recovery Boilers (DOE/AF&PA)	
Stress Corrosion Cracking of Composite Tubes (ORNL)	

The remainder of the report is organized to cover the status of each of the tasks shown in Table 1. The objectives and a brief summary of results from the DOE project and ORNL project on the composite tube cracking are covered at the end of this section.

Task 1

Long-Term Kinetics

Project Staff: Preet Singh, Greg Fonder

Project Funding: Member-Dues Funded Project

TASK OBJECTIVE:

To study long term (10,000 hours) kinetics of corrosion of C-steel in 1% H_2S at 400°C.

INTRODUCTION:

Boilers are designed to operate for many thousands of hours without replacing waterwall tubes. Between scheduled shut downs, the boilers generally operate for six months to an year (i.e. ~4400 to 8800 hours), depending upon individual mill maintenance plans. Most of the published data and previous laboratory tests at IPST were carried out at most a few hundred hours and usually much less than that. Alloy rankings are made based upon these short-term experiments as an estimate of remaining alloy life. An implicit assumption in this approach is that the kinetics do not change and the rate laws developed are constant. This has not been demonstrated for this application, and the data generated by discrete weight change measurements show gaps, which need to be better defined if accurate kinetic rate laws are a desired result. Continuous growth of the sulfide scale may result in two scenarios, in one, the growth stresses may increase with increases in the sulfide scale and the scale may spall-off, exposing a bare metal or a thin scale on the surface. In the other scenario, breakaway corrosion may be a result of depletion of the scale-forming element and cause the kinetics to change from parabolic to linear with a higher corrosion rate. This task was designed to determine whether these phenomenon are likely to occur in the recovery boiler environment by making continuous measurements of weight change over a 10,000-hour period.

EXPERIMENTAL PROCEDURE:

As was discussed in previous PAC reports, the upper portion of the Vycor reaction chamber extending above the furnace was wrapped in heating tape and insulated to ensure that the entire length is above the melting point of sulfur. This was done to avoid condensation of sulfur on chamber walls. A schematic diagram of the experimental arrangement is shown in Figure 1.

Prior to the test, the furnace was burned out to remove any deposits, which might have remained from previous tests. A coupon of known surface area was cleaned with acetone and weighed. Test coupon was prepared using the standard procedures discussed previously in PAC reports. The coupon was attached to the platinum chain and then carefully placed into the furnace. The furnace temperature was then slowly raised to the test temperature under a N_2 atmosphere. The coupon was kept under this atmosphere for a short time to allow the quartz spring to come to equilibrium. The flow of test gases was then started. The weight was monitored visually using a cathetometer by measuring the change in spring extension as a function of time. The spring constant of the quartz spring used is known, so the weight change could be calculated using Hooke's law.

RESULTS AND DISCUSSION:

Weight gain of the 1018 C-steel test coupon tested at 400°C in 1% H_2S + N_2 gas mixture are shown in Figure 2. These results show a classical sulfidation behavior where the initial corrosion rate was quite high and the rate of reaction slowed down with time due to formation of semi-protective sulfide sale on the surface. This change in the corrosion kinetics can be clearly seen in Figure 3 where log weight. Gain vs log time have been plotted. Value of the initial slope, corresponding to the initial corrosion rates, was around 1.0 which corresponds to the activation controlled reaction. The slope of the curve was less then 0.5 for the rest of the test results which indicates that the reaction rate had slowed down due to formation of a semi-protective sulfide scale on the surface. In this region, the reaction is controlled by the diffusion of the reactants through the sulfide scale.

Test specimens was retrieved after the test and the surface was optically examined. Micrographs in Figure 4 and 5 show that the scale was loose at certain places. There was no indication of scale spalling during the test. Some weight changes seen in Figure 2 were not due to scale spalling but due to the interruptions in the test to clean the observation window. Therefore, It is not very clear if the loose scale developed when the specimen was allowed to cool at the end of this test or they developed during the test.

SEM micrographs in Figure 6-8 were taken after mounting this specimen in epoxy and "dry" polishing to 15 μm finish. Specimen thickness after the test was 1.987 mm, as measured from the SEM micrograph shown in Figure 8. Whereas, the initial thickness of the test coupon was 3.00 mm. Therefore, the overall corrosion rate of 1018 C-steel at 400°C in 1% $H_2S + N_2$ gas mixture after 10,000 hours of exposure was 0.887 mm/year (34.9 mils/year, mpy).

The specimens were polished without any use of water to avoid diffusion of the scale constituents from one area to the other. This was necessary for the EDS analysis which was done on the sulfide scale to check its chemical composition and profile along the scale thickness. EDS analysis was performed in two different areas of the coupon, one area with detached scale, and other area where the scale was still attached. Results from the EDS study are shown in Figures 9-19. Corresponding areas of the EDS analysis are labeled in Figures 6 and 7. EDS analysis of the metal about 10μm away from the interface did not show any signs of internal corrosion. However, the scale near the metal/scale interface was iron rich as is shown from the EDS analysis in Figures 10 and 12 from two different areas. Scale near the gas/scale interface was rich in sulfur, as is shown in Figures 11 and 14. These results indicate that the sulfide scale formed on this test coupon is a non-stochiometric iron sulfide scale, which is comparable to the published data on sulfidation of iron at higher temperatures as well as with the reported analysis of the scale from lower furnace waterwall tubes in the recovery boilers.

Conclusions:

- Sulfidation of carbon steel at 400°C in 1% H_2S gas mixture follows a classic behavior where the initial scale growth rate is activation controlled whereas the further growth is controlled by the diffusion controlled corrosion reaction.
- There was no indication of scale spalling in this test during 10,000 hours of exposure.
- There was no indication of the internal sulfidation of the metal.
- Sulfide scale composition changes from a metal rich near metal/scale interface to a sulfur rich at the gas/scale interface.

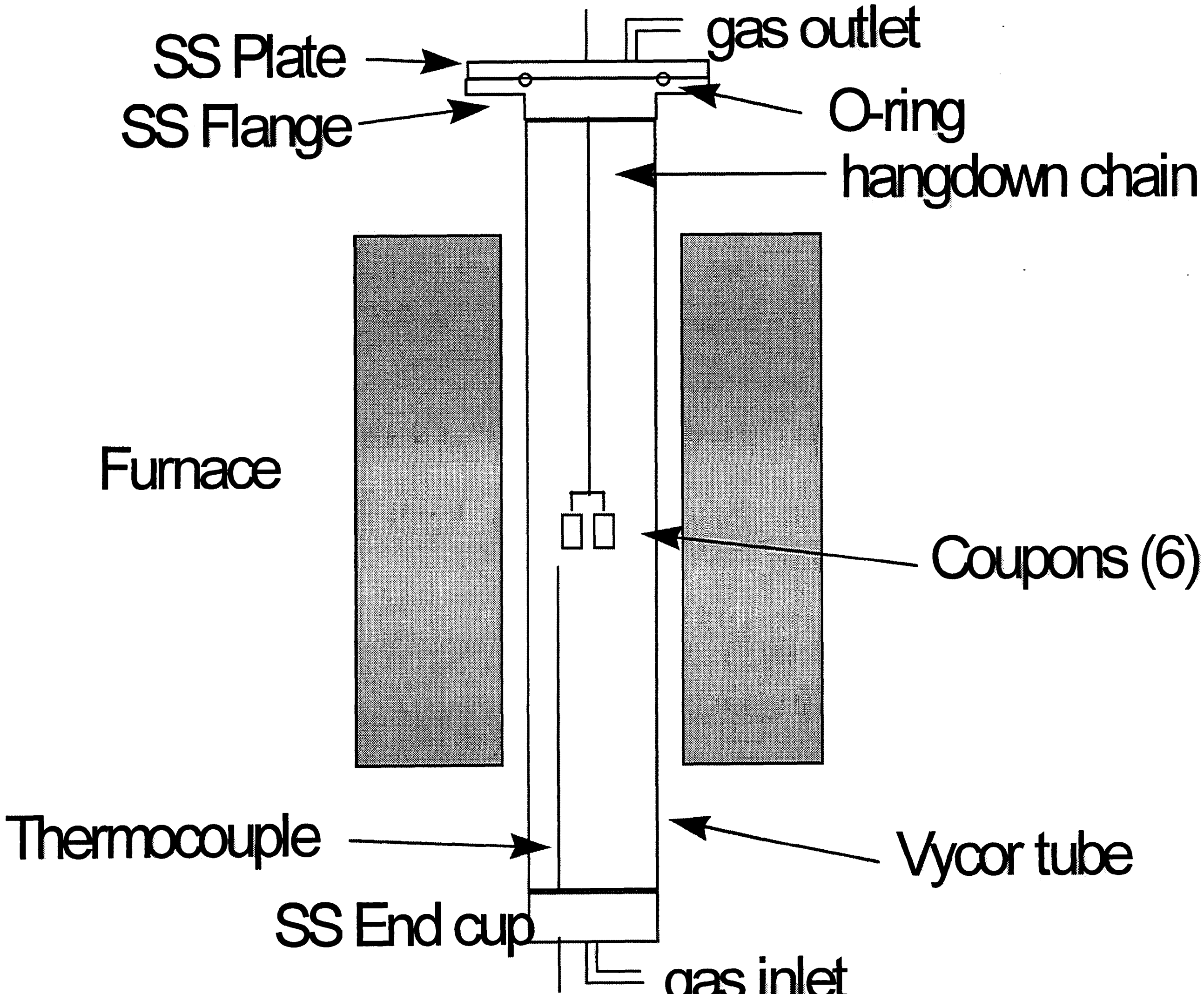

Figure 1. Experimental setup for long-term kinetic tests.

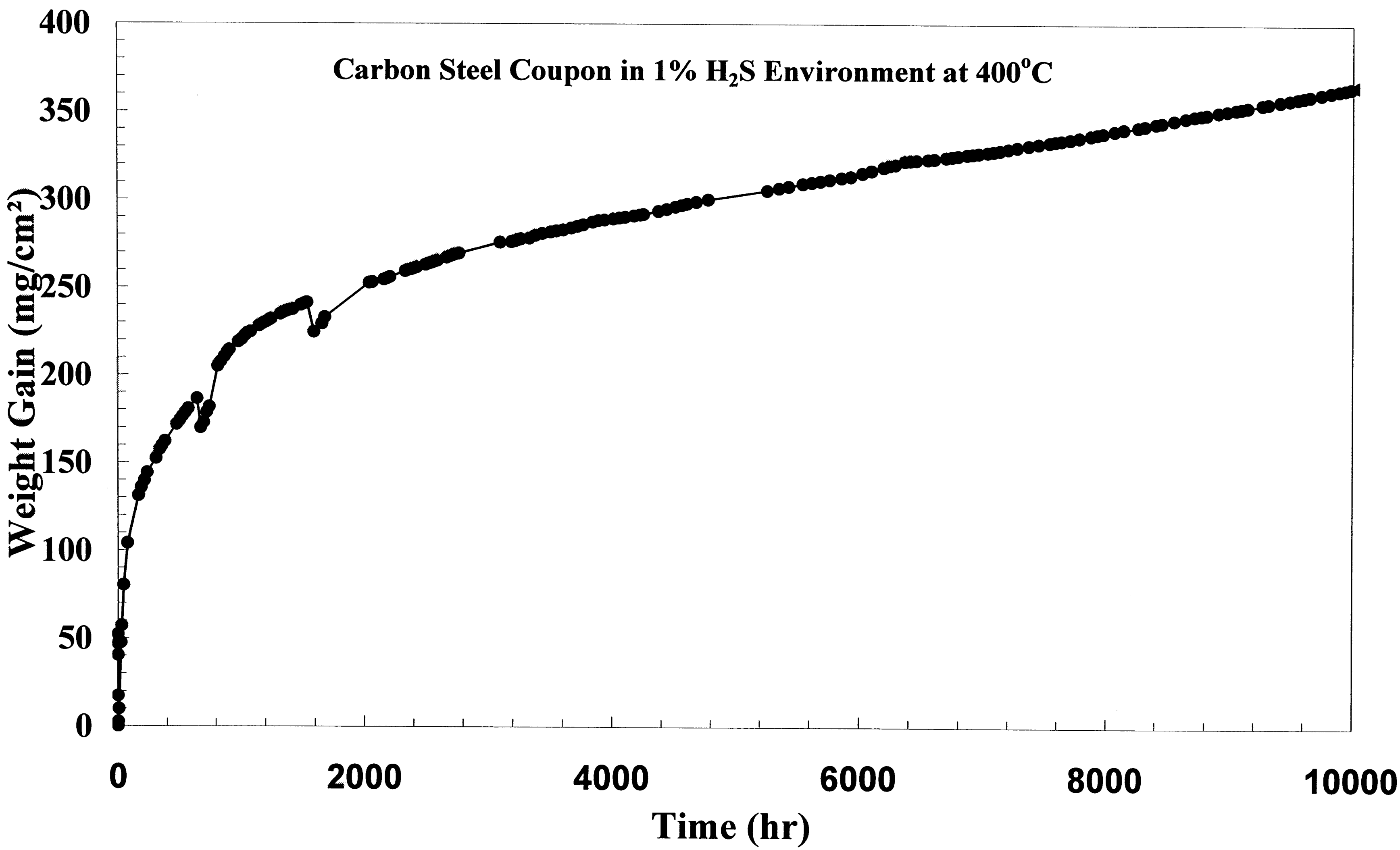

Figure 2. Weight change versus time for the long-term kinetics test.

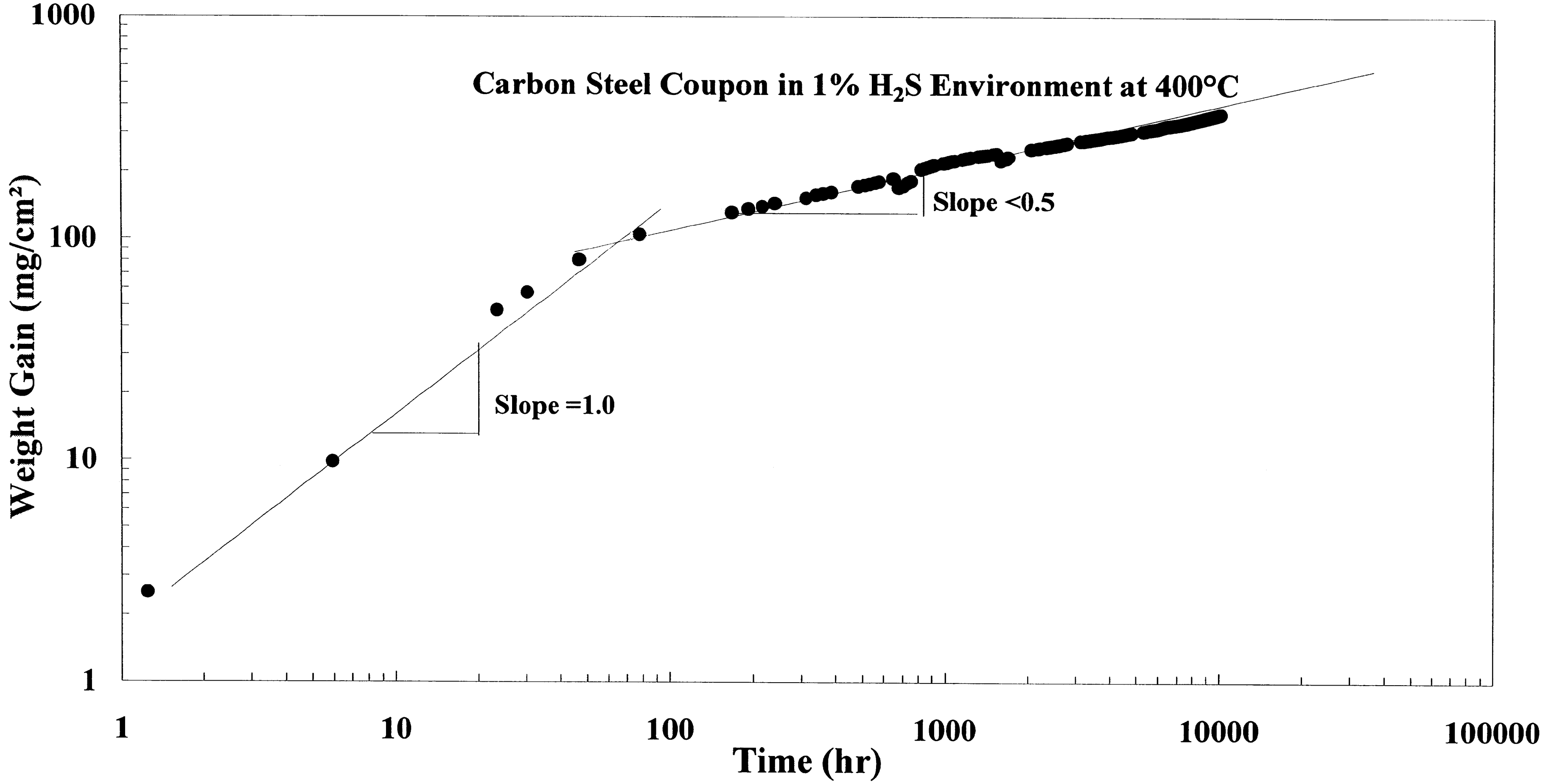

Figure 3. Weight change versus time for the long-term kinetics test.

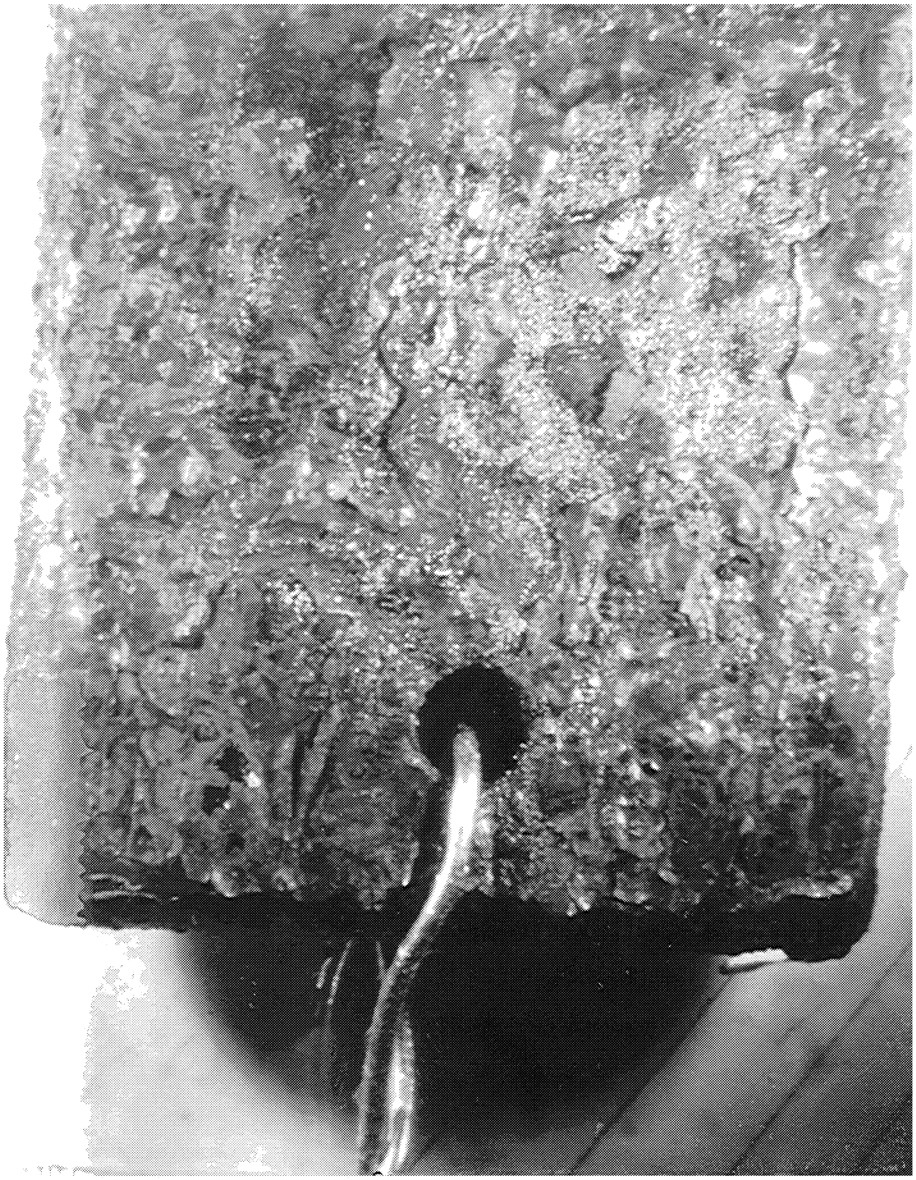

Figure 4 Optical micrograph showing the surface of the 1018 c-steel specimen tested at 400°C in 1% H2S +N_2 gas mixture for 10,000 hours. (x 10)

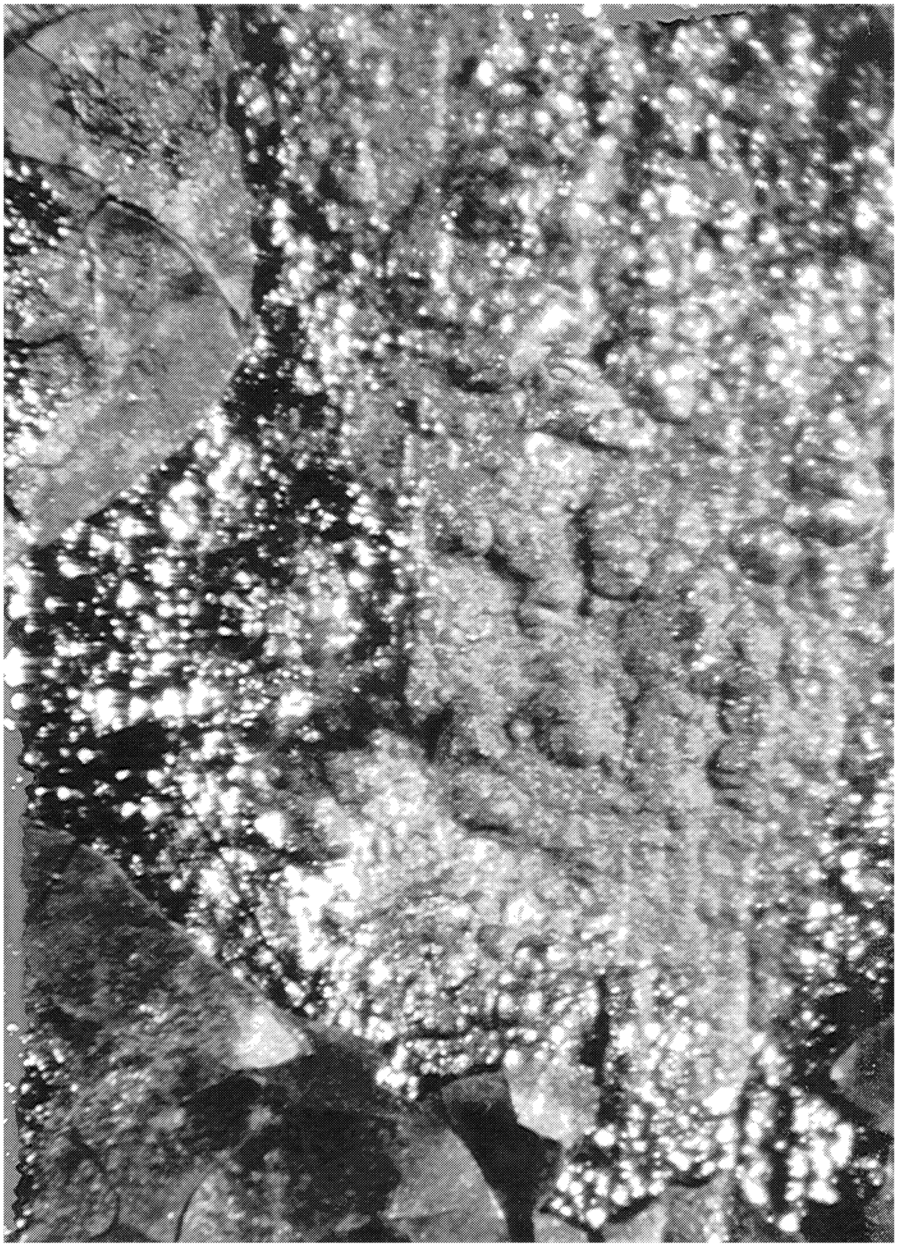

Figure 5 Optical micrograph showing surface of the 1018 c-steel specimen tested at 400°C in 1% H2S +N_2 gas mixture for 10,000 hours. (x 30)

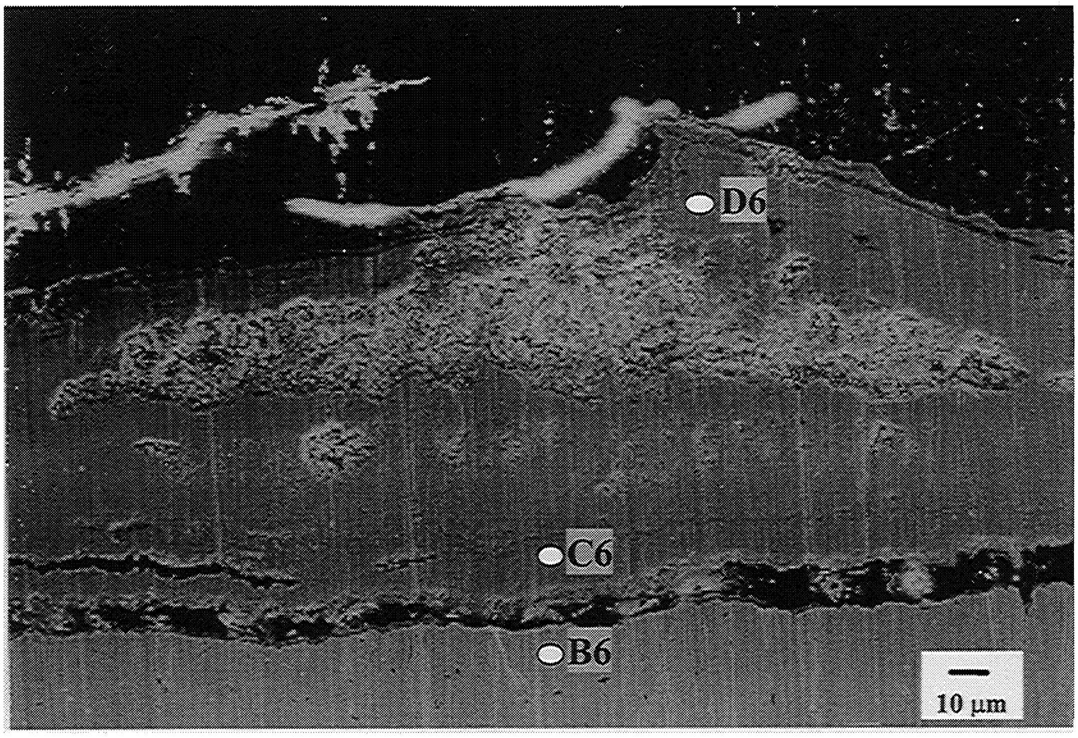

Figure 6 SEM micrograph of the detached scale formed on 1018 c-steel during 10,000 hour exposure at 400°C in 1% H2S +N_2 gas mixture. (x 400)

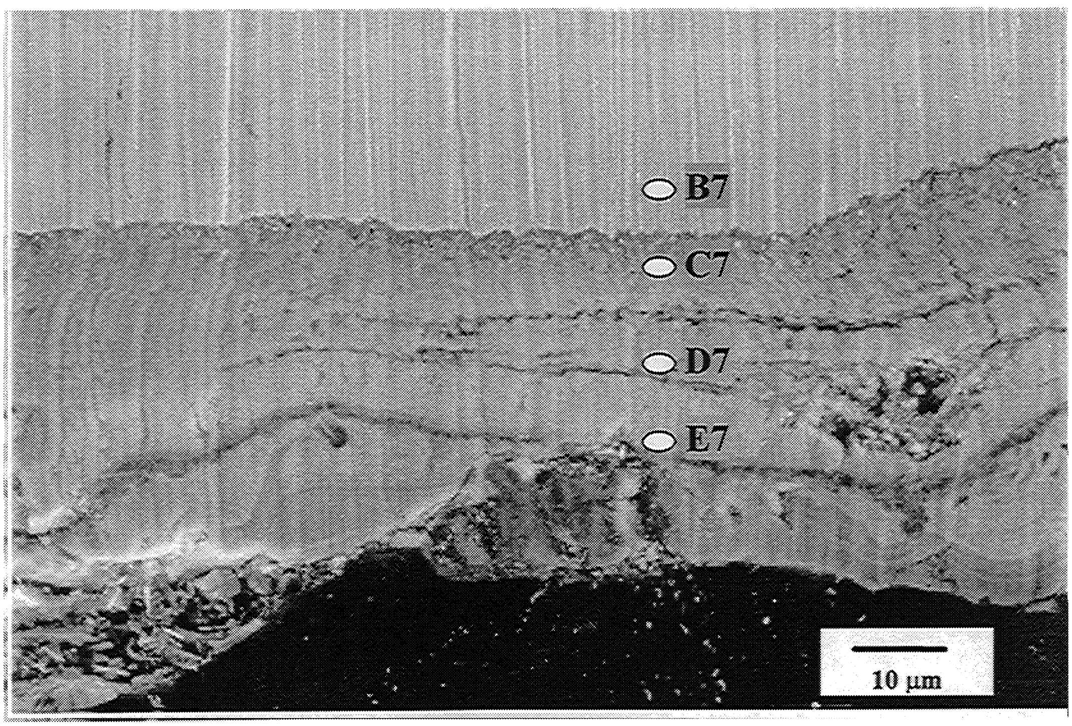

Figure 7 SEM micrograph of the attached scale formed on 1018 c-steel during 10,000 hour exposure at 400°C in 1% H2S +N_2 gas mixture. (x 1000)

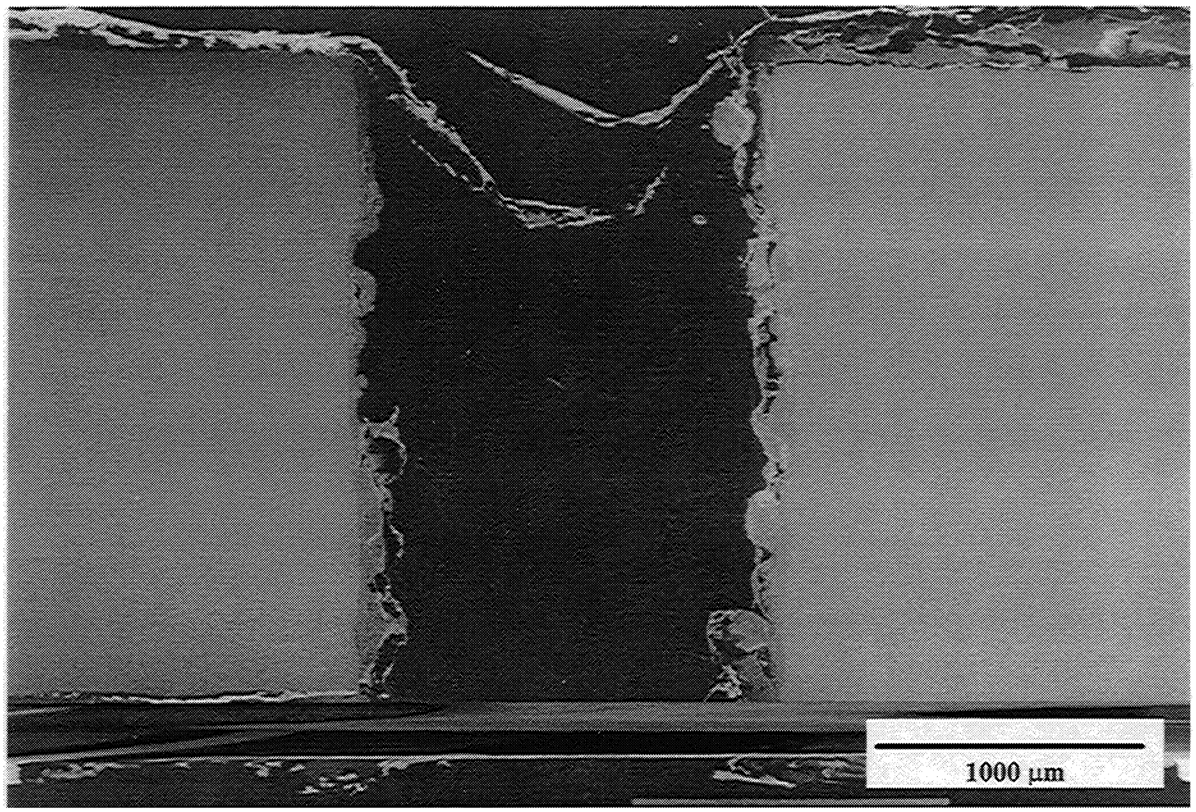

Figure 8 SEM micrograph of the 1018 C-steel exposed at 400°C in 1% H2S +N_2 gas mixture for 10,000 hours. (x 30)

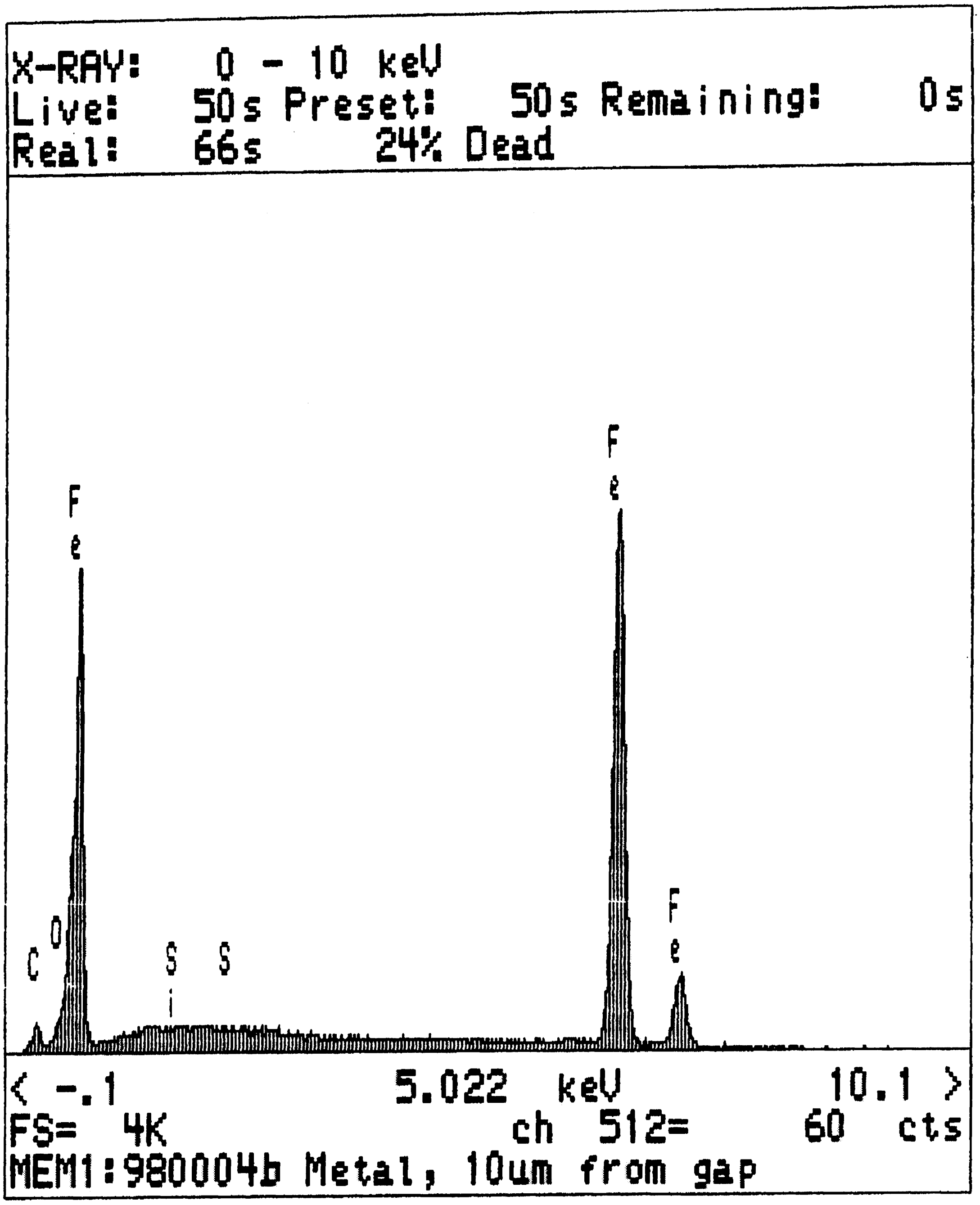

Figure 9 EDS results from the area "B" shown in Figure 6.

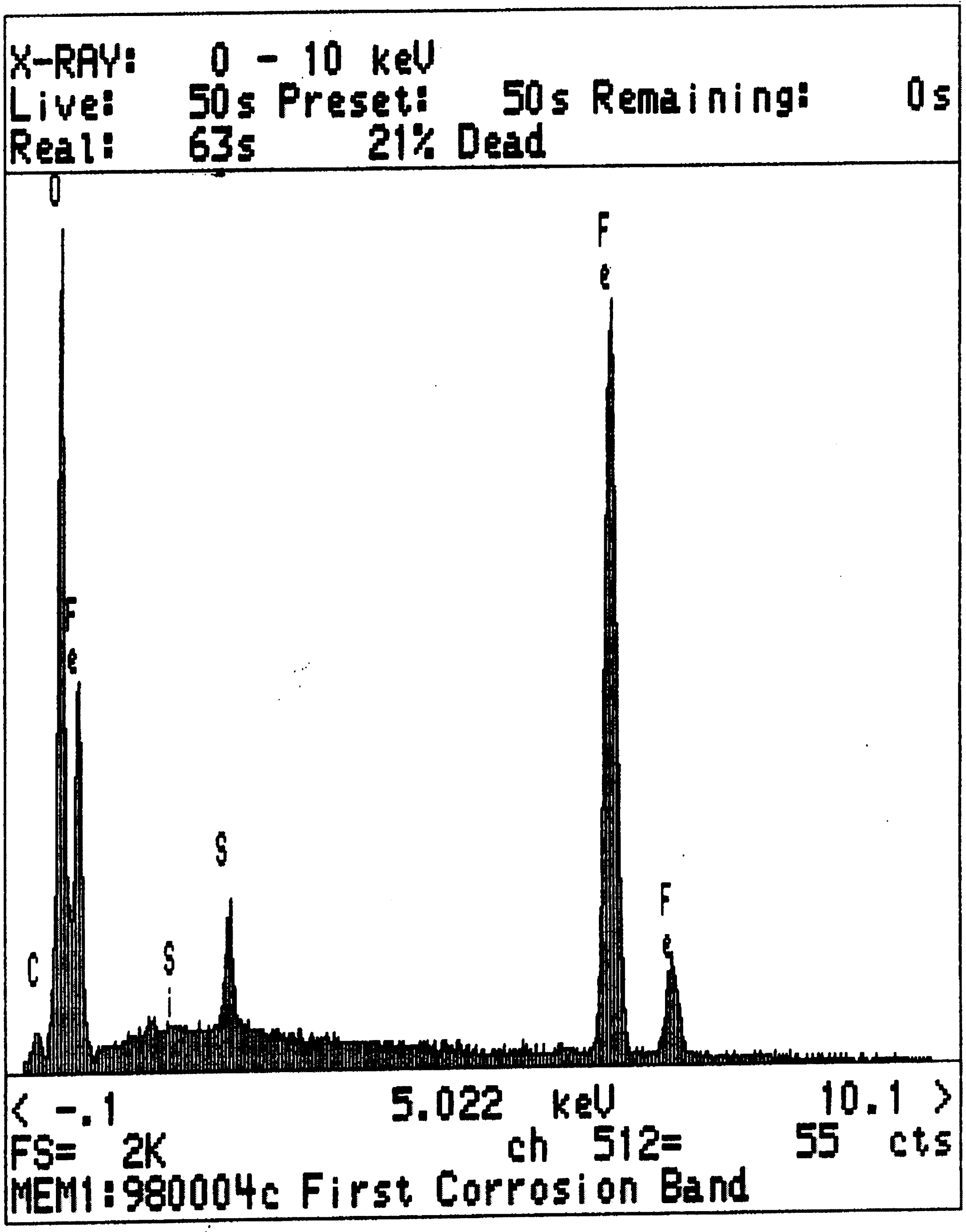

Figure 10 EDS results from the area "C" shown in Figure 6.

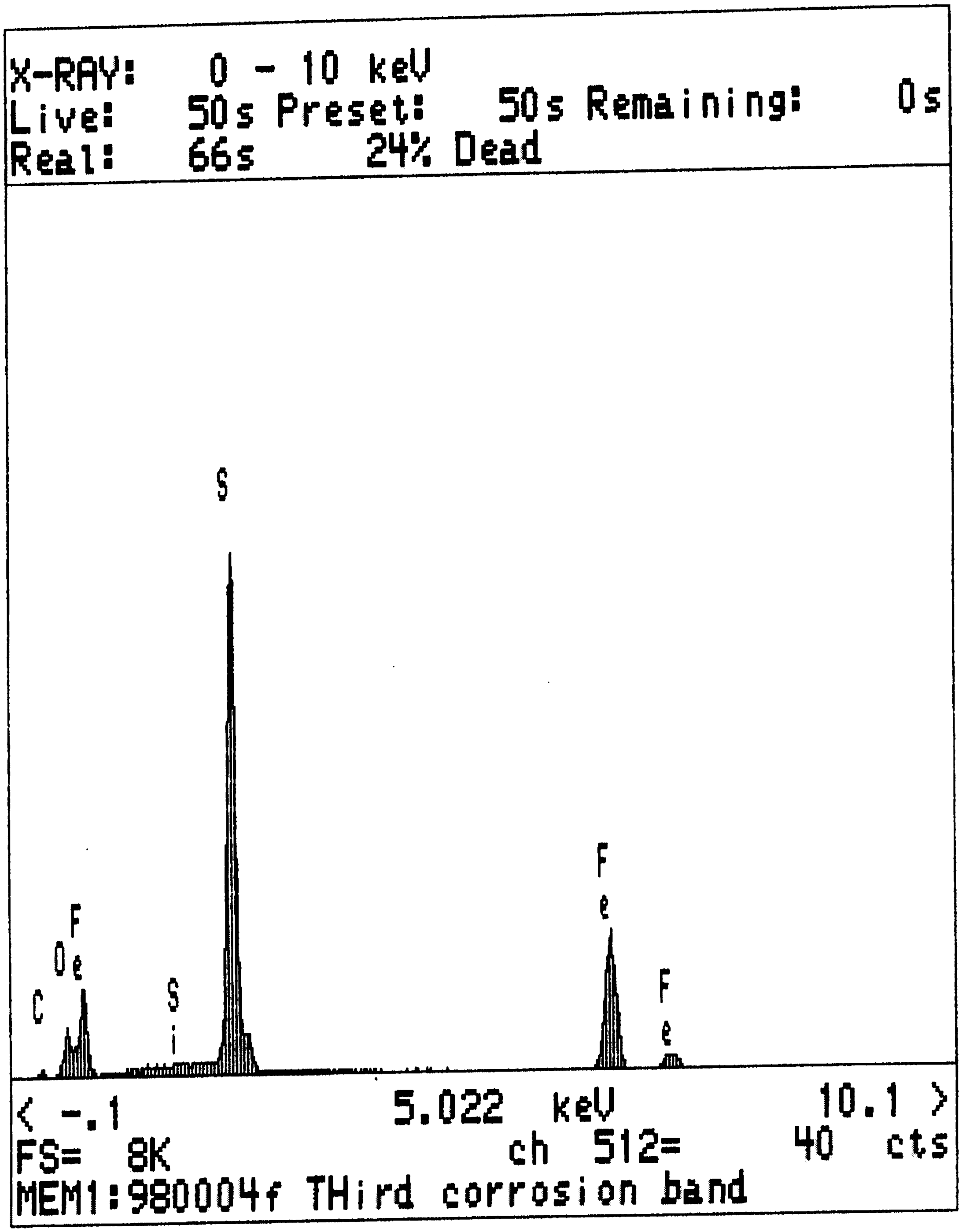

Figure 11 EDS results from the area "D" shown in Figure 6.

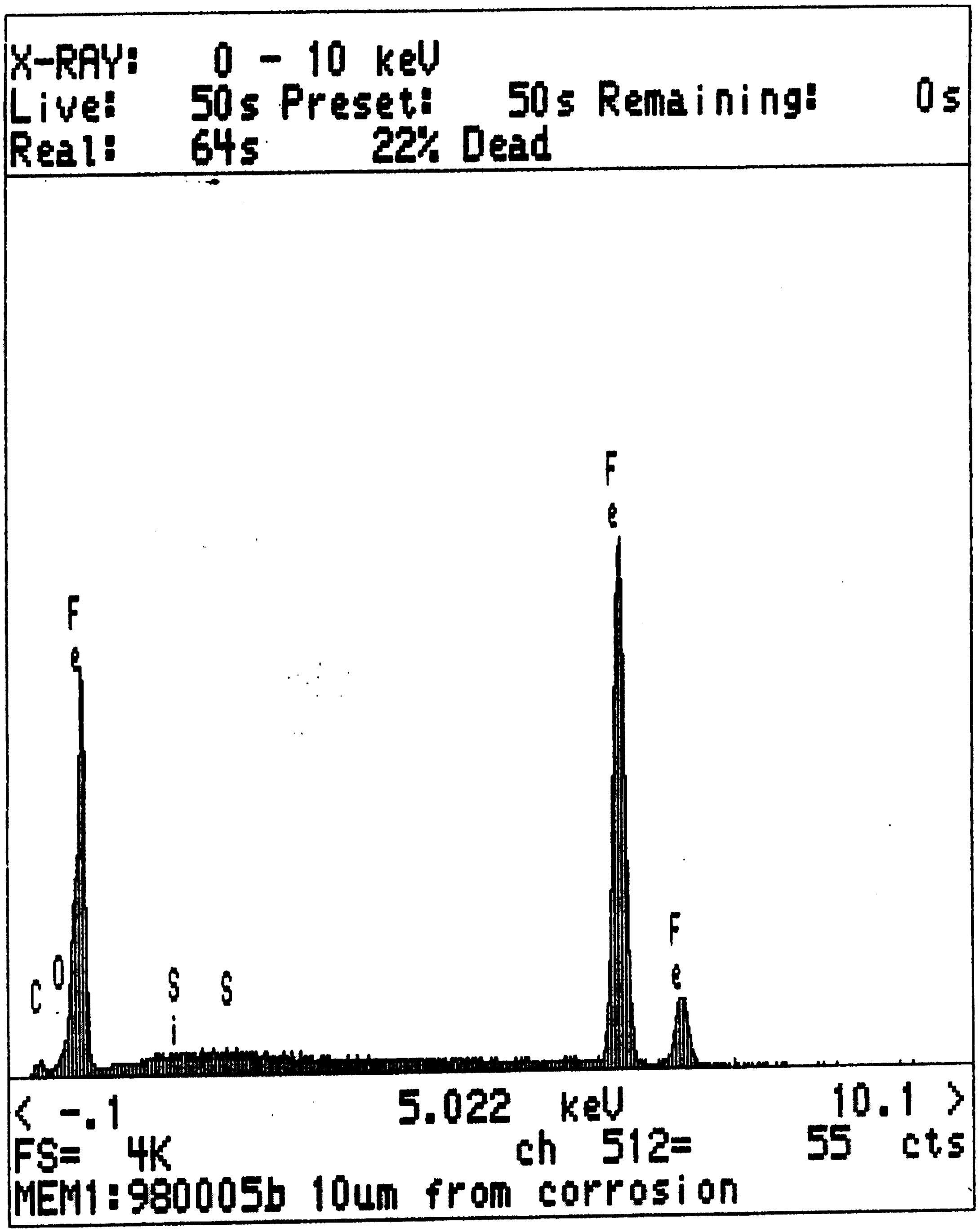

Figure 12 EDS results from the area "B" shown in Figure 7.

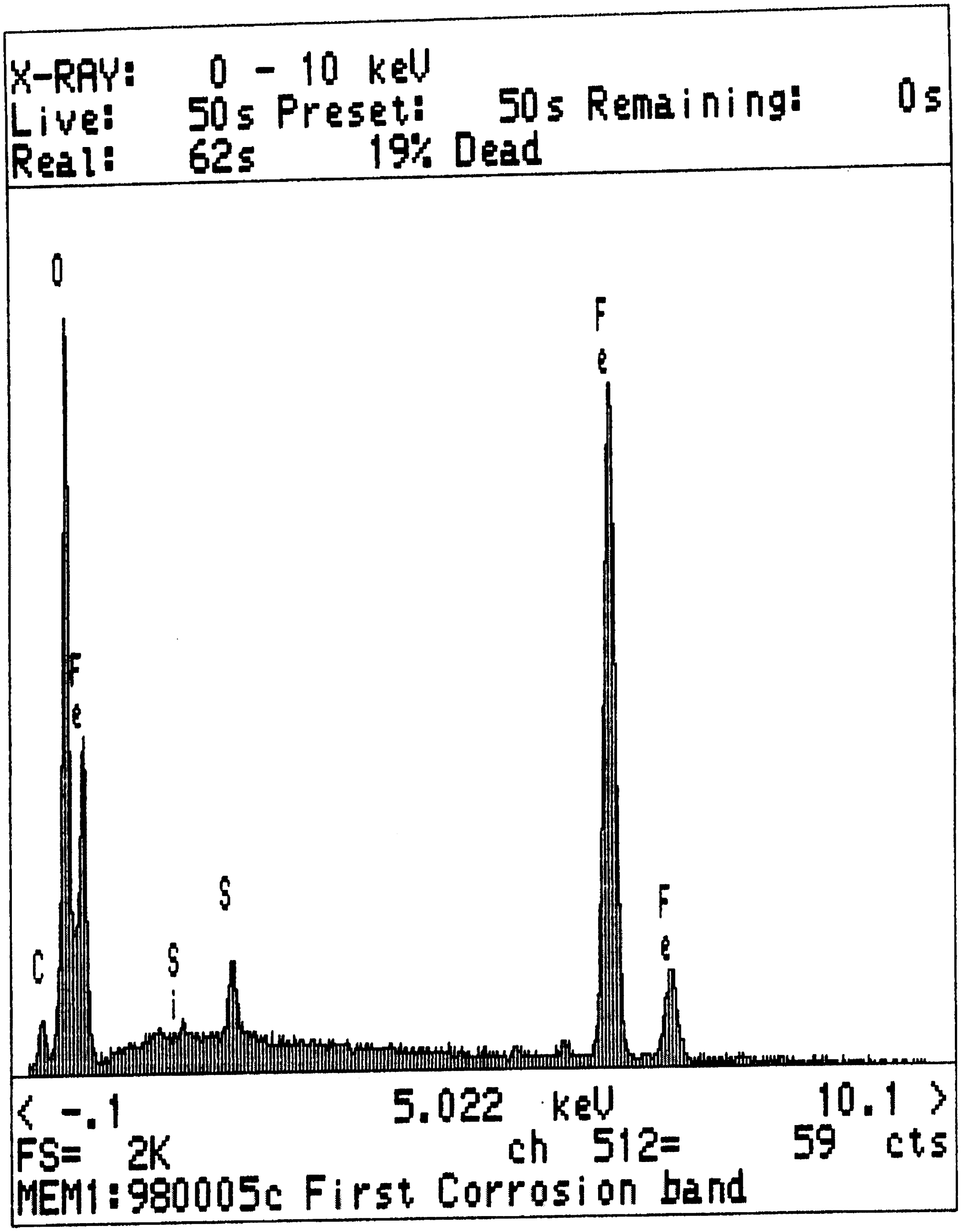

Figure 12 EDS results from the area "C" shown in Figure 7.

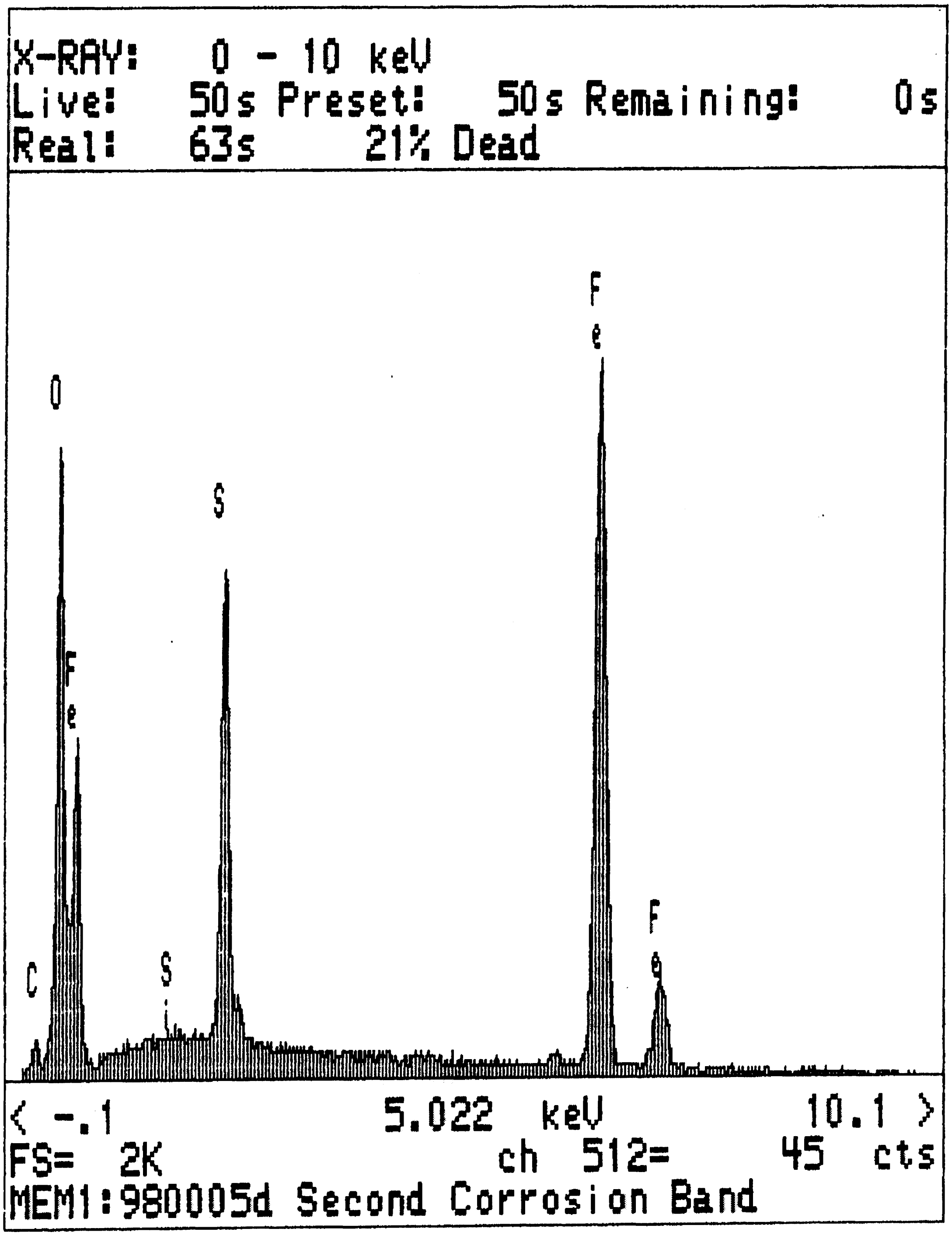

Figure 13 EDS results from the area "D" shown in Figure 7.

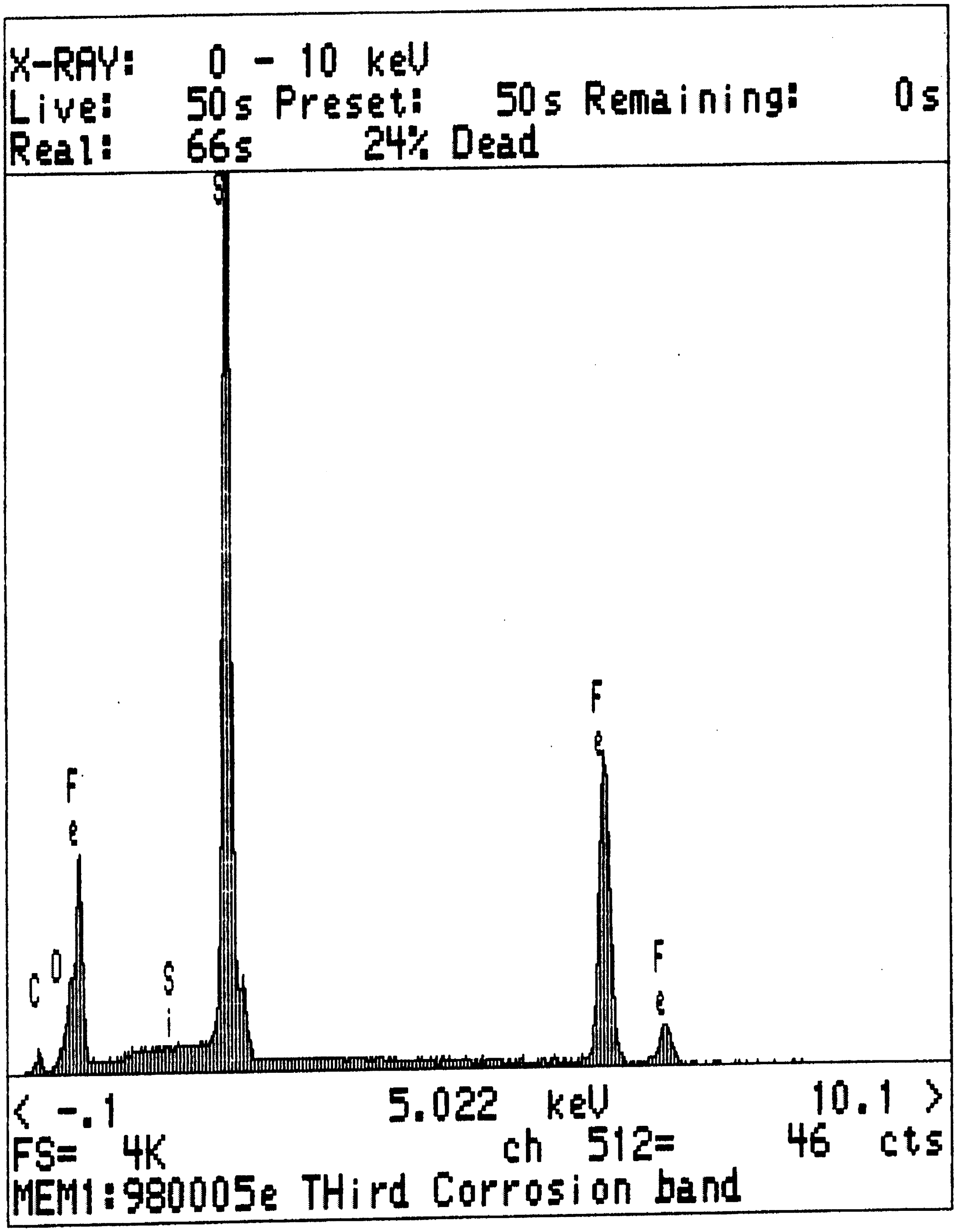

Figure 14 EDS results from the area "E" shown in Figure 7.

Task II

Gas/Smelt Interactions and Their Effects on Corrosion of SA-210 alloy

Project Staff: Preet Singh, Safaa Al-Hassan, Greg Fonder, Sloane Stalder

Project Funding: DOE funded project, and member-dues funded

OBJECTIVES:

To generate basic understanding of gas/smelt interactions and their effects on the corrosion processes involved in lower furnace environments

INTRODUCTION

Previous work has indicated that the presence of smelt changes the corrosion rate and corrosion characteristics considerably in typical recovery boiler environments. There are limited published data available to show these effects in the recovery boiler environments.

One of the highest rates of corrosion in the recovery boilers occurs on the fireside of water wall tubes in the lower furnace area. This area is generally under reducing conditions. Smelt, a frozen mixture of salts, accumulates on the furnace tubes and reduces the water wall tube temperature and thus reduces the metal wastage. For the corrosion reactions to continue on the tubes of kraft recovery boiler, the bulk gases from the furnace must pass through the frozen smelt on the tube and react with tube material, as is shown schematically in Figure 15. This interaction might produce mixture of gases with concentrations different from the bulk gas mixture. Sulfide scale on the tube surface grows by the reaction of the resultant gas mixture with the tube material at the scale/smelt interface. The interaction of the bulk gas mixture with the smelt components is an important step in the water wall tube corrosion in the lower furnace area. Most of the previous tests carried out at IPST and by other researchers were done by dipping test coupons in the smelt. Whereas in present study the gases passed through the smelt and the test specimens were exposed to the resultant gases. This was done to separate the effects of gaseous changes and other factors like local molten salt corrosion of the specimens which is expected in cases where the test coupons are in touch with the smelt.

EXPERIMENTAL PROCEDURE

SA-210 carbon steel specimens were cut from 5-cm-OD tube and burnished according to the standard procedure described in AF&PA /95 report. The specimen dimensions were 2.5 cm x 1.8 cm x 0.5 cm. Coupons were cleaned with acetone and weighed before they were hanged on a glass tree and placed in the reaction tube. Smelts were prepared by mixing their constituents for at least six hours in an enclosed bottle, making sure that the constituents were not exposed to air during this procedure. Smelt was loaded in 300-mL, 304 stainless steel cylinder. The original gas mixture (1% H_2S + N_2) was passed through the smelt and the resultant gas mixture was taken to the reaction tube where the coupons were exposed to this mixture. A schematic drawing of the experimental apparatus is shown in Figure 16. The temperature of the smelt cylinder was controlled to ± 5°C of the test temperature at which the test coupons were exposed in the reaction tube. After the test was finished, specimens were taken out of the reaction tubes, sulfide scale was removed by sandblast and the specimens were weighed to an accuracy of 0.1 mg. The smelt compositions used in these tests are shown in Table II.

RESULTS:

Two sets of tests with either 25 or 50 g of smelt #1 were carried out at 400°C for three time periods (4, 8, 24 hr). Two specimens were tested for each test conditions. The change in weight loss of SA-210 is shown in Figure 17. The weight loss of SA-210 in 1% H_2S is 0.8 mg/cm^2 and 1.4 mg/cm^2, respectively, for the tests carried out for 4- and 24-hours. That gave a corrosion rate of 0.03 mg/cm^2.hr. Using 25 g of smelt, the weight loss increased by 12%, 13%, and 8% for 4, 8, and 24 hour tests, respectively, when compared with similar tests done in 1% H_2S gas environment. Testing 50 g of smelt #1 resulted into an increase in the weight loss of 25%, 4%, and 26% respectively, for 4, 8, and 24-hour test, respectively. Furthermore, using two cylinders to load 50-g weight of smelt (25 g in each cylinder), the weight loss increased by 29% and 2% in 8- and 24-hour tests, respectively, compared to similar tests without smelt. A larger amount of smelt was not tested for concerns that it might affect or block the gas flow. The scale was removed mechanically (low-pressure sandblast) to calculate the weight loss. Using 50-g weight of smelt #2 in 4- and 24- hour tests decreased the weight loss by 28% and 9% compared with tests in only 1% H_2S. Smelt #3 increased the weight loss by 4% and 11% in the same time interval, as is shown in Figure 18.

Effect of Sodium Chloride

Tests were also done to study the effects of chlorides in a recovery boiler environment due to introduction of chloride rich effluents in the recovery cycle. Tests were carried out in the presence of smelt #4-6, which are smelts #2-3 with 2% or 4% of NaCl. Smelt compositions are given in Table II. The use of 50 g of smelt #4 decreased the weight loss by 46% and 15% in 4- and 24-hour tests, respectively, when compared with similar tests done in 1% H_2S gas only. Whereas, tests using 50 g of smelt #5 showed a decrease in the weight loss by 19% and 24% in the same time periods.

Effect of Oxygen

Thermodynamic calculations suggest that NaCl may greatly influence the weight loss in the presence of oxygen gas. Oxygen gas is known to increase the weight loss to a maximum at approximately a 1:1 ratio with H_2S. The addition of 1% O_2 to 1% H_2S gas increased the weight loss to 1.43 mg/cm^2 in 4 hour and 3.8 mg/cm^2 in 24-hour test, which corresponds to 0.0985 mg/cm^2.hr. That means that the addition of 1% O_2 to the gas mixture increased the weight loss by 83% and 170% in 4 and 24 hour tests, respectively, when compared with similar tests in 1% H_2S gas only, as is shown in Figure 19. Thermodynamic calculations suggested that the addition of oxygen to H_2S pushed the reaction towards higher elemental sulfur production from H_2S gas. Using 50 g of smelt #6 in 1% O_2 + 1% H_2S decreased the weight loss by 17% and 48%, when compared with similar tests without smelt in the same time periods, as is shown in Figure 20. The effect of NaCl here is not very clear, which may be because of its low concentration in the smelt. However, tests with 50 g of smelt #7 increased the weight loss for 24-hour-time period to 135% and 300% in two different tests. Gas flow was blocked in the later tests due to sulfur condensation in the cold areas of the tube. Repeating the same tests with 10, 30, 50 g of NaCl increased the weight loss by 218%, 135%, and 136%, respectively, as shown in Figure 20.

DISCUSSION

Assuming that hydrogen sulfide reacts with smelt components individually, thermodynamic calculations indicate that the reaction of Na_2CO_3 with H_2S to produce Na_2S, H_2O, and CO_2 has a positive free energy. Similarly, Na_2SO_4 produces Na_2S, H_2O, and SO_2 with positive free energy, as is illustrated in Equations (1-2).

$H_2S+Na_2CO_3=Na_2S+H_2O+CO_2$ $\Delta G = 15 - 4$ kcal/mol at 300-600°C (1)

$4H_2S+3Na_2SO_4=3Na_2S+4H_2O+4SO_2$ $\Delta G = 44 - 28$ kcal/mol at 300-600°C (2)

Thermodynamic calculations were done with data for pure compounds and do not predict interactions between the compounds. However, smelt #1 (rich in Na_2CO_3) increased the corrosion, in general, as the weight of smelt and test time were increased, while smelt #2 (rich in Na_2S) decreased the weight loss compared to weight loss for only 1% H_2S environment. Furthermore, smelt #3 (rich in Na_2SO_4 or poorer in Na_2S than smelt #2) increased the corrosion compared with tests in smelt #2. Results suggest the smelt components (Na_2CO_3, Na_2SO_4, and Na_2S) interact with H_2S thereby changing corrosion rates for carbon steel, although the change is not significant. The smelt after experiment appeared to develop a crust with the color changing from white to yellow. Although exact reactions due to gas/smelt interaction are not clear, our results indicate that the smelt base components are not inert and interactions do occur which may change gas composition based on the reactions. Work is continuing to analyze the resultant gases by gas chromatography, which will increase our understanding of the gas/smelt reactions and explain some of the corrosion test results.

Effect of Sodium Chloride

Concerns with the NaCl are that reactions of NaCl with hydrogen-containing gases may result in HCl formation under recovery boiler operating conditions. HCl at recovery boiler operating temperatures is known to be very harmful, even for 304 stainless steel. Applying the same principle that H_2S reacts individually with the smelt components, thermodynamic data give positive free energy for the reaction of NaCl and H_2S that produces Na_2S, as in Equation (3).

$H_2S + NaCl = Na_2S + 2HCl$ $\Delta G = 53 - 44$ kcal/mol at 300-600°C (3)

Testing smelt #4 decreased the weight loss by 46% and 15% in 4- and 24-hour tests, respectively. Whereas, smelt #5 decreased the weight loss by 19% and 24% in the same test periods.

Effect of Oxygen

However, the addition of 1% oxygen to the gas mixture increased the weight loss significantly (by 83% and 170% at 4- and 24-hour tests, respectively). Oxygen reacts with H_2S to produce H_2O and S_2 with a significant negative free energy as is shown in Equation (4).

$$O_2 + 2H_2S = 2H_2O + S_2 \qquad \Delta G = (-)74 - (-)73 \text{ kcal/mol at } 300\text{-}600^{\circ}C \qquad (4)$$

Stelling and Vegeby [*Pulp and Paper Magazine of Canada*, **70**, T236, 1969] reported that corrosion from H_2S and O_2 increases pointedly when the conditions are changed to favor the formation of sulfur. This is consistent with our observations in the present study as the presence of oxygen leads to higher production of sulfur and that caused the subsequent condensation of sulfur on the cold tube surfaces. The present study indicated a very significant increase in the corrosion rate of SA-210 specimen in 1% H_2S + 1% O_2 gas mixture. However, tests with smelt #6 reduced the weight loss of carbon steel coupon when compared with that done without smelt in 1% H_2S + 1% O_2. Plumley, et al. [*TAPPI*, **49** (1), 72A, 1966] tested smelt constituents individually in nitrogen and air (source of O_2), and reported that tests in Na_2S showed a fourfold increase in the weight loss in air compared to the similar tests done in nitrogen. Furthermore, Fonder and Ahlers [IPST-PAC project report #3628, 1991] reported that the addition of 5% NaCl to smelt increased the weight loss by 57%. Results from both reports were obtained by dipping the coupons into the smelt, which is different from the way the test coupons were exposed in the present work. Test coupons dipped in smelt may also undergo molten salt corrosion if some localized low-melting-point phases form at the surface of the test coupon at high temperature. Conversely, the test coupons in the present set of experiments only are only exposed to the effect of resultant gas changes. The recovered smelt at the end of testing smelt #6 was found to develop a stronger crust and close to orange color compared to yellow crust for test in only H_2S. This hard crust may stop gas permeation and gas/smelt interactions.

Tests with smelts #7 (only NaCl) were done using 50 g and the results show that the weight loss increased tremendously. The reaction of H_2S, O_2, and NaCl produces HCl with high negative free energy, as is shown in Equations (6-7).

$$2O_2 + 2NaCl + H_2S = 2HCl + Na_2SO_4\ ;\ \Delta G = (-)142 - (-)127 \text{ kcal/mol at } 300\text{-}600^{\circ}C \quad (6)$$
$$1.5O_2 + 2NaCl + 2H_2S = 2HCl + Na_2SO_3\ ;\ \Delta G = (-)85 - (-)75 \text{ kcal/mol at } 300\text{-}600^{\circ}C \quad (7)$$

However, gas flow in these tests with 1% H_2S + 1% O_2 and NaCl was blocked due to sulfur condensation on the cold areas of tubes. The results of tests with 10 g of smelt #7 suggest that 125 g of smelt (on basis of 4% NaCl in smelt) may be needed to produce similar effects of NaCl presence in smelt. However, this does not consider the interaction of other smelt components with initial gases. Tests with 125 g of smelt cannot be done in the present setup due to concern that the gas flow will be blocked in such a test. However, smelt with a very high NaCl content (higher than the maximum practical NaCl content) should be tested. That will allow us to see if the interaction of NaCl and other smelt components with $H_2S + O_2$ gas mixture results in a more corrosive gaseous mixture as is predicted by simple thermodynamic calculations.

CONCLUSIONS

1. The presence of smelt increased the weight loss of SA-210 carbon steel by 25% in the case of smelt #1 (80% Na_2CO_3, 12% Na_2SO_4, 8% Na_2S), but decreased the weight loss by 9% in the presence of smelt #2 (65% Na_2CO_3, 15% Na_2SO_4, 20% Na_2S) in 24-hour tests when compared to similar tests conducted in 1% H_2S gas mixture only. Weight loss in the presence of smelt #3 was between the weight loss results of smelt #1 and smelt #2. The smelt developed a crust with yellow color.
2. The presence of O_2 in the gas mixture (as in 1% H_2S + 1% O_2 gas environment) increased the weight loss by 170% in the 24-hour test compared to similar tests done in 1% H_2S gas.
3. The addition of NaCl to smelt by percentage (2 to 4% in smelt), which may be expected in recovery boilers, did not change the weight loss significantly when the tests were done with 1% H_2S as well as 1% H_2S + 1% O_2 gas mixture. The smelt developed a strong crust with orange color.
4. Using NaCl only (without smelt) increased the weight loss of SA-210 carbon steel in 1% H_2S + 1% O_2 gas mixture by 217% when compared to test results without salt.

Table II. Chemical composition of smelts used in this work.

SMELT	CHEMICAL COMPOSITION
Smelt #1	80% Na_2CO_3, 12% Na_2SO_4, and 8% Na_2S
Smelt #2	65% Na_2CO_3, 15% Na_2SO_4, and 20% Na_2S
Smelt #3	65% Na_2CO_3, 27% Na_2SO_4, and 8% Na_2S
Smelt #4	Smelt #2 + 2% NaCl
Smelt #5	Smelt #3 + 2% NaCl
Smelt #6	Smelt #3 + 4% NaCl
Smelt #7	100% NaCl

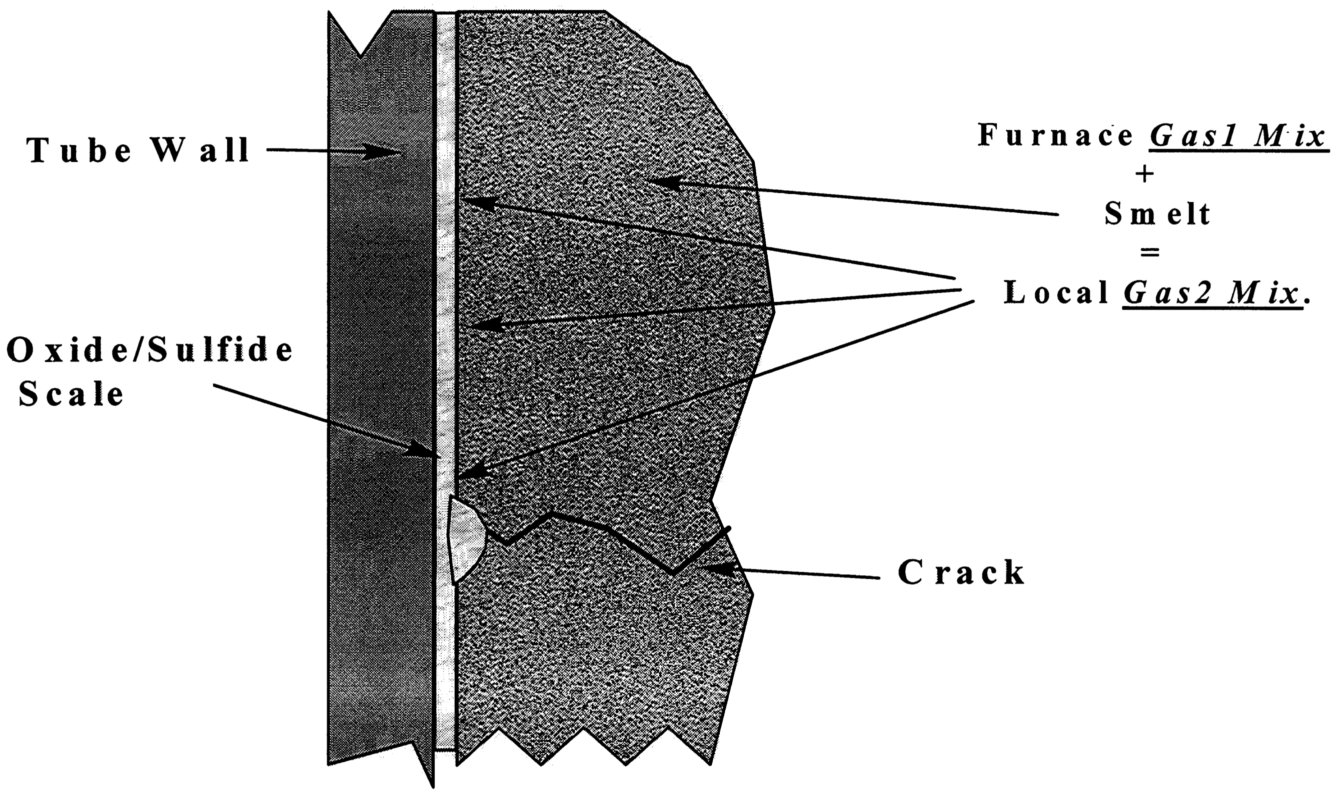

Figure 15. Schematic diagram showing access of the reactant gas mixtures from the lower furnace of the recovery boiler to the water wall tube surfaces through frozen smelt.

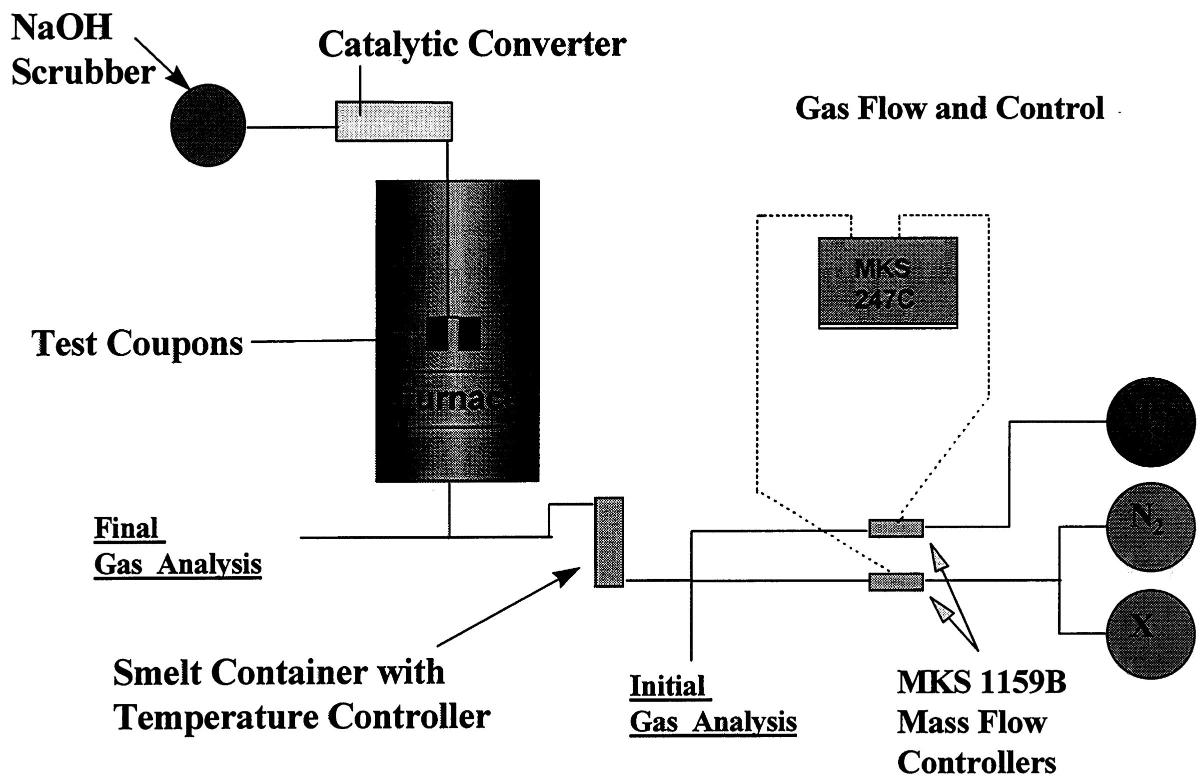

Figure 16. Schematic diagram of the experimental apparatus used in the present work.

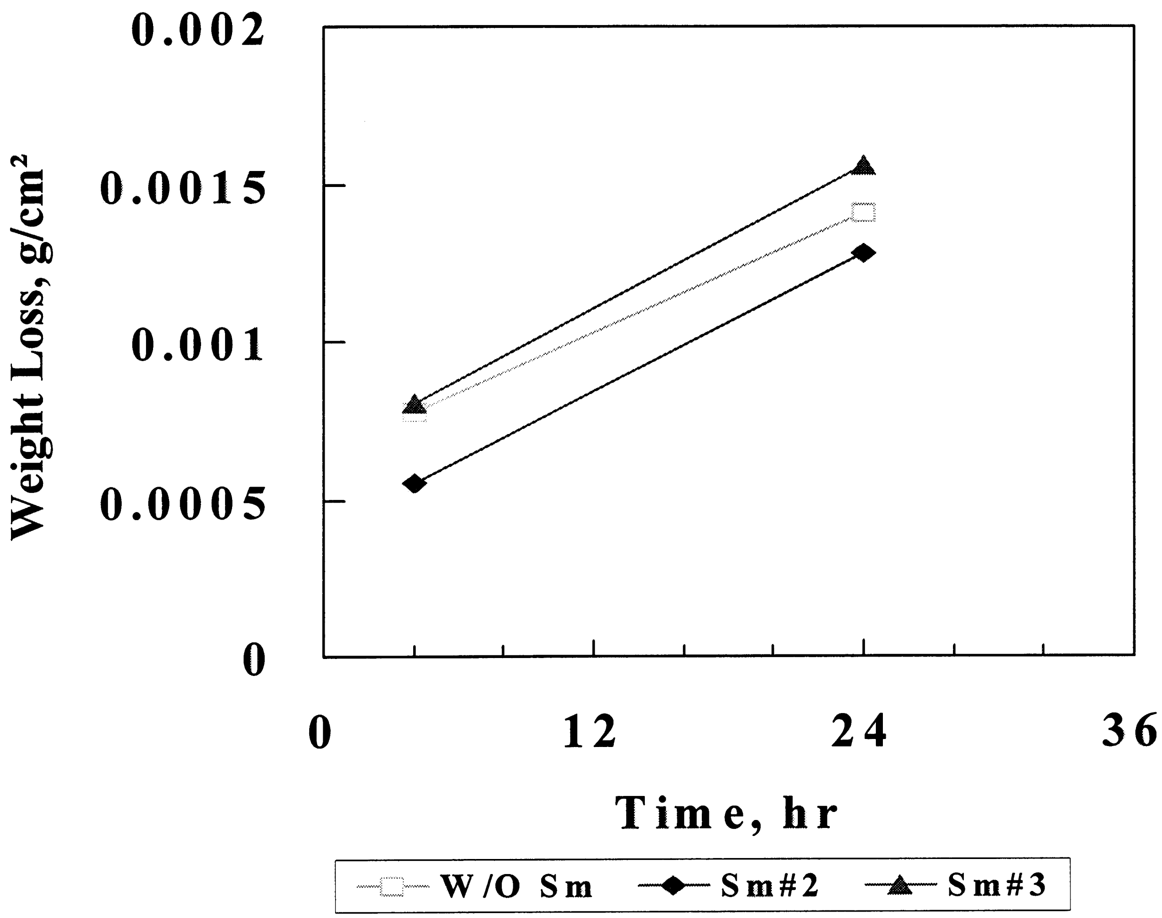

Figure 17. The weight loss of SA-210 carbon steel in 1% H_2S and smelt #1 at 400°C.

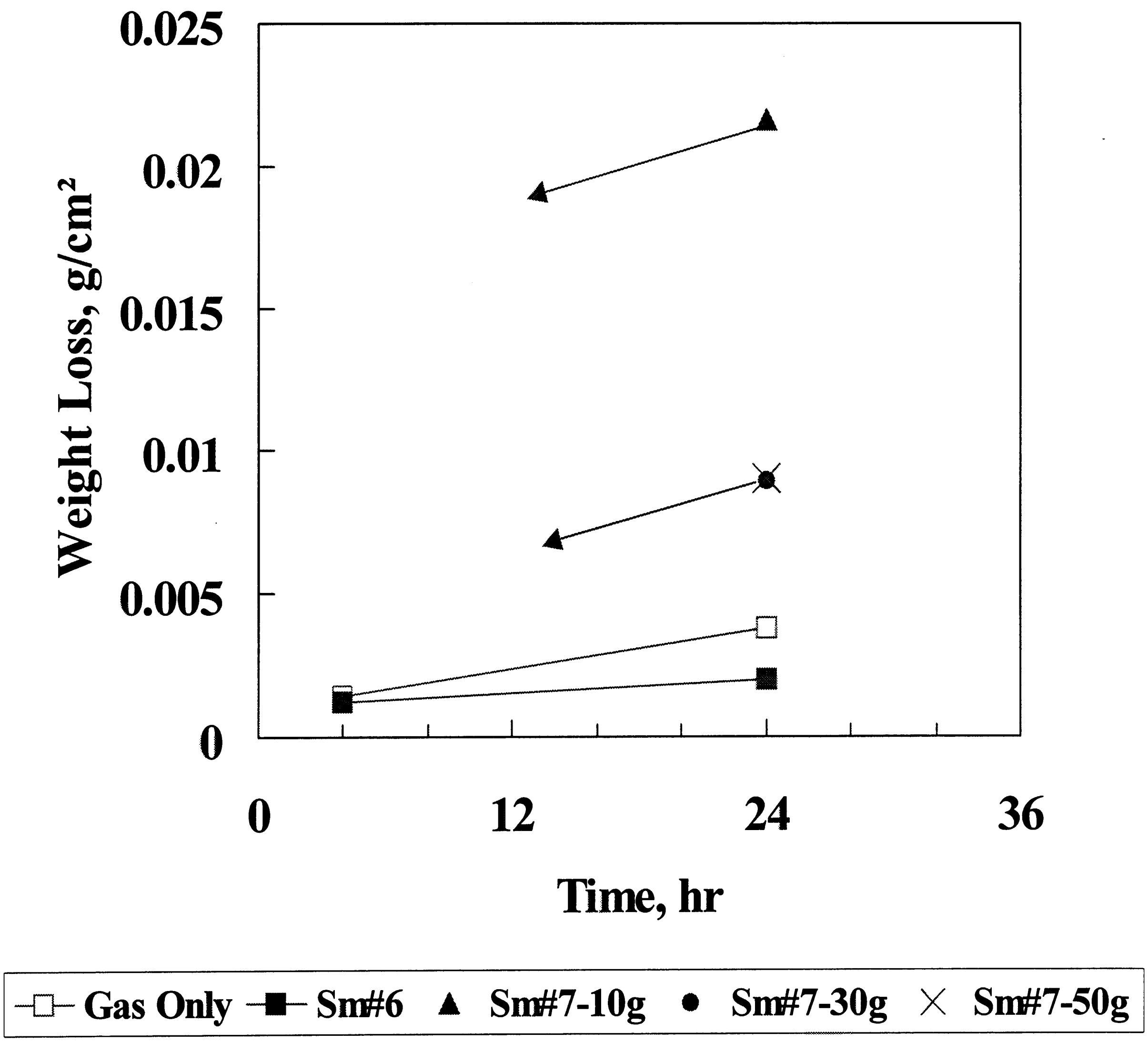

Figure 18. Weight loss of SA-210 carbon steel in 1% H_2S and 1% H_2S + 1% O_2 gas mixtures at 400°C.

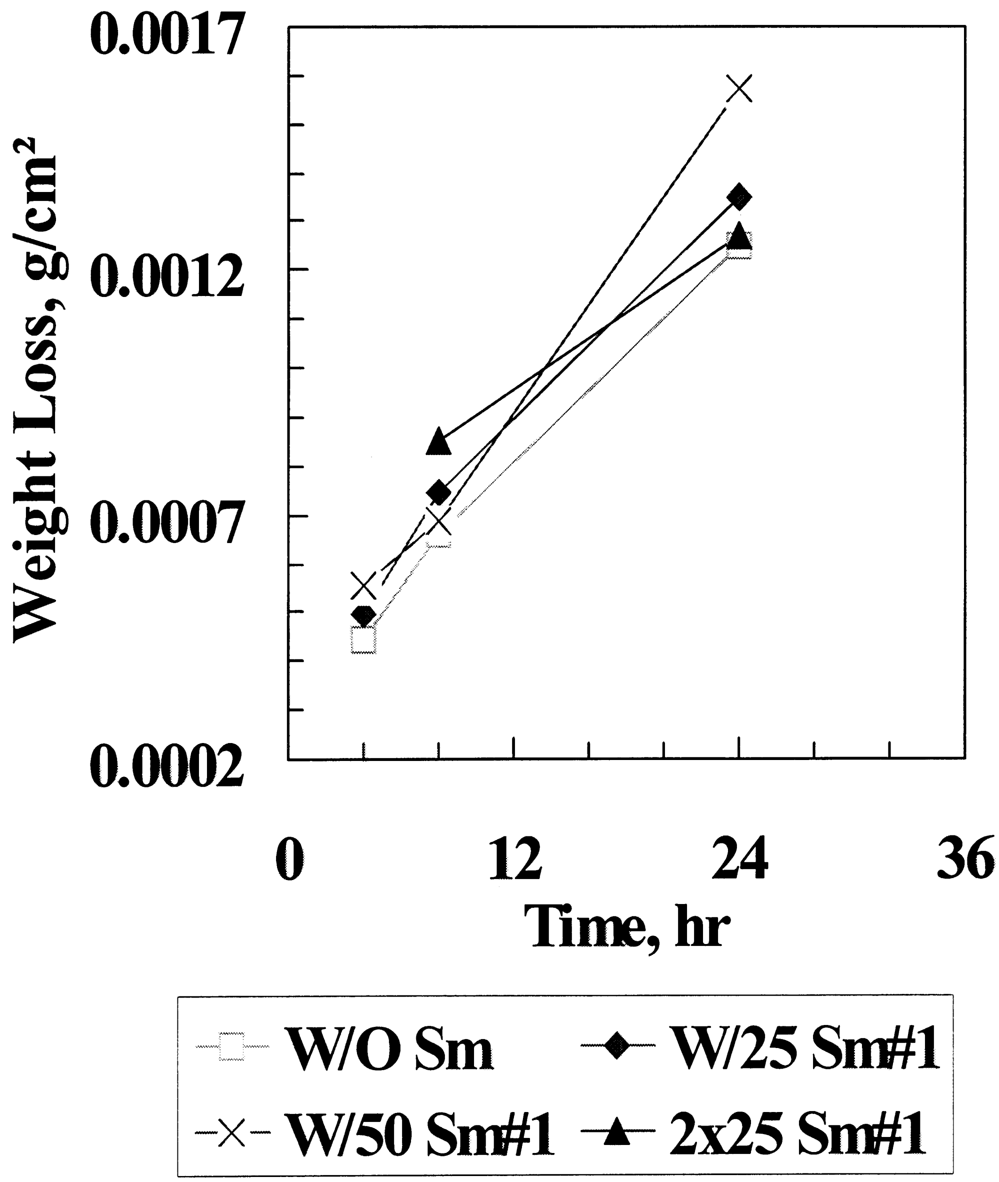

Figure 19. The effect of oxygen on the weight loss of SA-210 carbon steel in 1% H_2S + 1% O_2 at 400°C.

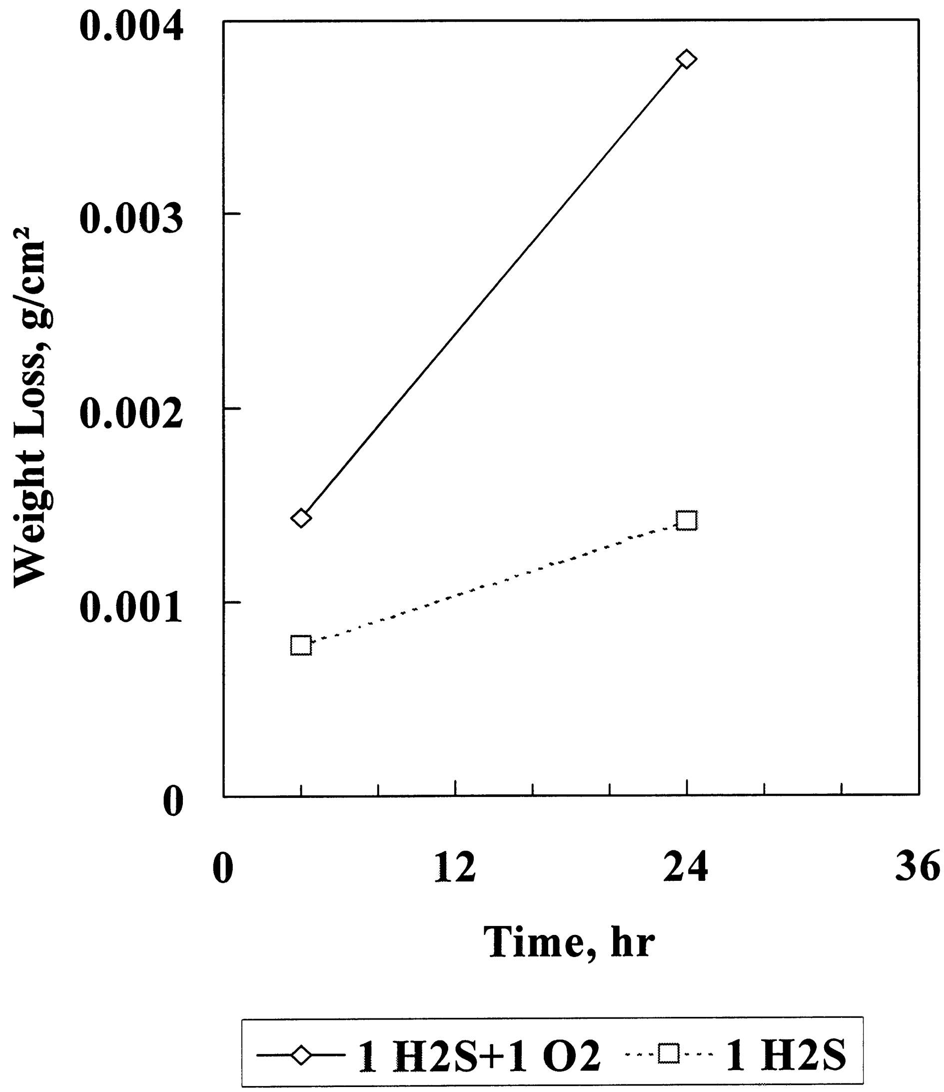

Figure 20. The effect of smelt #6 and different weights of smelt #7 on the weight loss of SA-210 carbon steel in 1%H_2S+1% O_2 at 400°C.

Corrosivity Monitoring of Kraft Recovery Boilers

Externally Funded by DOE

Project Title:	Corrosivity Monitoring of Kraft Recovery Boilers
Project Staff:	Preet. Singh, G. Fonder, S. Al-Hassan, Sloane Stalder, Jamshad Mahmood
Project Funding:	DOE (Cost-share:- IPST, and AF&PA)

Summary of 1995-97 results

The focus of this project is to develop an extensive corrosion kinetics database as well as to develop a corrosion monitoring device or a device to measure conditions that control corrosion in an operating recovery boiler. The benefit of such an approach is that it will allow operators to predict or explain the impact of decisions prior to damaging boiler components. The project is divided into four phases, with each phase is designed to last for one year.

Corrosion kinetics database:
Phase I and II (1995-97) involved designing and developing a corrosion kinetics database, a detailed study on the most promising candidates for corrosion measurements, and laboratory testing of measurement techniques. The corrosion kinetics database was developed at IPST with two main objectives in mind:

(1) to collect the published information on corrosion kinetics, relevant to the recovery boilers, in a form of database,

(2) to develop a database which may be used with the indirect corrosion measuring techniques (e.g. thermocouples and/or gas sensors) for the prediction of corrosion in kraft recovery boilers.

Work on the development of database design as well as data collection and entry was finished by October 1997. The database was designed using a commercial Microsoft Access® package. This database is an icon-driven, user-friendly, windows-operated system. Published corrosion kinetics data from gas industry, coal gasification, pulp and paper industry, and other industries, as well as from other fundamental studies were collected. An on-line database search as well as back-referencing were used to identify and collect the relevant published papers for the corrosivity database. The database already has over 12,000 data points, representing data from more than 300 materials and

400 environmental conditions relevant to the recovery boiler fireside environments. Two papers showing the capabilities and use of this database for corrosion prediction and material selection for recovery boilers have been submitted for publication. One paper was submitted for the International Recovery Boiler Conference and the other for the International Symposium on Corrosion Problems in Pulp and Paper Industry.

The published literature covers most of the relevant alloys and environmental conditions similar to kraft recovery boilers. However, there are a significant number of gaps in the published data on the environmental/material combinations, which are very important for this database. To fill-in these gaps, experiments were conducted at IPST to generate this data. Three different types of tests were identified; Isothermal tests, tests with different smelt compositions, and cyclic temperature tests. Data generated from these tests was also entered into the database. Experimental results have provided us with a better understanding of the effects of various factors on the corrosion in the lower furnace of kraft recovery boilers.

Smelt/Gas interactions and their effects on waterwall tube corrosion:

In Phase II, preliminary work was started at IPST to generate an understanding of the effects of smelt on the gaseous corrosion of carbon steels. Results from this effort have already been discussed in section on Task II of the member-dues funded project. These efforts will be extended into Phase III (1997-98) of the DOE project so that we can predict the local environments at the interface by knowing the smelt and bulk gas compositions in a particular area of the recovery boiler.

Effects of temperature excursions on waterwall tube corrosion:

Water wall tube surfaces in the Kraft Recovery Boilers experience temperature excursions. Those excursions can increase the corrosion rate in the localized areas of the recovery boiler. Occasional temperature excursions can influence the corrosion of the boiler tubes on fireside by one or combination of the following mechanisms;

1 increase in diffusion controlled reaction rates and overall sulfidation reaction rate,
2 microcracking of the semi-protective sulfide scale due to thermal stresses and increased reaction kinetics,
3 molten salt corrosion (if the molten smelt is in touch with the fireside tube).

When the temperature excursions are more than the melting point of smelt then the molten salt corrosion will increase metal wastage significantly. However, excursions above the melting point of frozen smelt in the lower furnace areas have not been reported.

In present series of tests, SA-210 carbon steel samples were tested in 1% H_2S gas mixture tested at 320°C, with temperature different number and locations of temperature spikes to 480°C. The results from these tests have shown that once damaged by the thermal excursion, the sulfide scales do not effectively heal in this system during the post-spike exposure. Results from this study have a very important implications from the recovery boiler point of view that even a couple of infrequent spikes, which cause scale damage through microcracking, followed by a long post-spike exposure will lead to very high corrosion rate. The corrosion of water wall tubes due to infrequent thermal spikes may even be higher than the isothermal exposure at higher temperature of spike.

General conclusions from this series of experiments are as following:

1. Thermal excursions generally leads to higher sulfidation rates compared to equivalent test without spikes.
2. Scale damage may depend upon scale thickness, history of exposure, and spike location.
3. A sulfide scale damaged due to thermal excursion may not heal and may lead to very high corrosion rate in the post-spike exposure. Even a couple of infrequent spikes, which lead to scale damage, may lead to even higher corrosion rates than the isothermal tests at upper temperature of the spike.

Two Papers related to the experimental results from this study have been submitted for the publication in the the International Symposium on Corrosion Problems in Pulp and Paper Industry proceedings.

Corrosion Monitoring Probe Developments:

Electrical resistance probes were developed and constructed at IPST. Probes were tested under different environmental conditions relevant to recovery boilers. The main objective of this study is to check the feasibility of this technology for corrosion measurement, and to check the parameters such as stability of signal, reproducibility, etc. SA210 coupons were also tested along with the probe to compare the probe output-signal with the coupon weight loss results. Tests were performed at different temperatures between 320 °C and 570°C. Most of the tests were done in a % H_2S gas environment; however, a few probes were also tested in a 1% SO_2 environment to simulate upper furnace areas. Two different types of active elements (i.e., c-steel and 304 stainless steel) were used to construct these probes. Although, we used a very basic wheatstone bridge circuit without any amplification, in this study, the electrical resistance probe results were very reproducible. The correlation between the results from the weight loss tests and the probe output-signal was very good.

Most of resources in phase III will be devoted towards Electrical Resistance probe design, testing, and strategies for the installation of probes in the recovery boilers. Installation design efforts will concentrate on water-wall-flush IPST-ER probes for kraft recovery boilers. More work will be carried out in phase III to study the effects of scale composition in extreme environmental conditions, and the design effects such as active element alloy composition on the probe output-signal. Testing of these probes under different environmental conditions and comparison of probe output-signal with the weight loss tests will help us to improve this probe for in-situ corrosion monitoring in kraft recovery boilers.

Monitoring of corrosive environments in recovery boilers:

A new subtask has been added to this project for year 1997-98 and the work for this subtask involves field monitoring of the environments in two recovery boilers. Candidate boilers with a known corrosion history will be selected based on the AF&PA TAG recommendations. Environmental variables, local gas composition, tube surface temperature, and smelt composition will be studied. Real-time bulk gas composition will be analyzed in different areas of the boiler with a "Portable" gas chromatograph with an on-line gas sampler. Gas sampling probes, which can fit through 0.5-inch holes have been designed. These probes will also have a thermocouple to measure the temperature at the sampling site. The temperature of water wall tubes will be continuously measured in the selected areas of the recovery boiler by installing a number of surface-mounted thermocouples on the crown of tubes. These measurements will be related to measurements of membrane temperature obtained by (long-lasting) thermocouples mounted on the cold side of the membranes. Smelt samples will also be collected from the tube surfaces in selected areas and will be analyzed.

Stress Corrosion Cracking of 304L Stainless Steel in Kraft Recovery Boilers

Project Title: Stress Corrosion Cracking of Composite Tubes in Kraft Recovery Boilers
Project Staff: Preet Singh, Jamshad Mahmood
Project Funding: Oak Ridge National Laboratory

OBJECTIVES :

To study environments in kraft recovery boilers that may cause stress corrosion cracking of 304-L stainless steels.

INTRODUCTION :

Composite tube cracking in kraft recovery boilers is one of the major safety concerns of recovery boilers. Results of the ORNL investigation and other published results indicate that the composite tube cracking in kraft recovery boilers may be due to SCC. It is not clear as to what environments are responsible for these failures.

An exploratory project was started at IPST to investigate the possible stress corrosion cracking (SCC) mechanisms which can operate on the composite tubes. This project is now funded by Oak Ridge National Laboratory as a part of the DOE funded project on composite tube cracking, going on at ORNL. The following are the main objectives of the project at IPST:

1) To investigate tendencies of various wash water compositions, and different constituents of wash waters, to cause SCC of 304-L stainless steel.
2) To study other environments in the recovery boilers during the shut down condition which may cause stress corrosion cracking of 304-L stainless steel.
3) To study the microstructural changes occurring in the composite tubes during operation and their effects on SCC susceptibility of 304-L stainless steel in recovery boiler environments.

Summary of experimental results:
A test matrix was designed to study the stress corrosion cracking susceptibility of 304-L stainless steel in different wash water compositions at different temperatures. In this program, 304-L tensile specimens are being tested in different environments using slow

strain rate test method. In this type of tests, the tensile specimens are exposed to the given test environment and the specimens are strained at a constant extension rate corresponding to a very slow (generally $\leq 1x10^{-6}/s$) initial strain rate. Specimens are strained at a given extension rate till they fracture. There are different parameters which can be compared for different tested specimens (i.e. % Reduction in area, % Elongation, Crack velocity, etc.). However, the presence of visible stress corrosion cracks on the specimen surface and/or fracture surfaces are of prime importance in these tests.

Test environments used so far in this study include the artificial wash water compositions as shown in Table III. However, other chemical environments were also tested and are listed in Table IV. Tests were carried out at different temperatures. Tests conducted at temperatures above 100°C were carried out in special slow strain rig with an autoclave made out of Hastalloy-C. The test specimens were electrically isolated from the test rig in all tests. All specimens were tested at a constant extension rate giving an initial strain rate of $2x10^{-6}/S$

Table III Composition of artificial white waters used, so far, in this study

Chemicals	Artificial WW#1	Artificial WW#2	Artificial WW#3
Sodium Carbonate	65%	60.50%	33.333%
Sodium Sulfate	17%	14%	
Sodium Sulfide	15%	15%	33.333%
Sodium Thiosulfate	2%	5%	
Sodium Chloride	0.50%	5.00%	
Sodium Hydroxide	0.50%	0.50%	33.333%

Results from these tests are listed in Table IV. All 304L specimens tested at 200°C in different wash waters have shown severe stress corrosion cracking susceptibility. Most of the specimens tested at lower temperatures did not show SCC susceptibilities in the environments tested so far. However, specimen no. 19, listed in Table IV, had SC cracks when tested in concentrated Na2S + NaOH solution at 100°C. Tests in different environments, corresponding to typical wash water compositions or their constituents, are continuing.

Anodic polarization tests were conducted on 304L specimens in white water # 1 and #3. Based on our results from these electrochemical tests, a limited number of slow strain rates were conducted with applied potential. None of these tests have shown any SC cracks so far. Slow strain rate tests with applied potential are in progress, but, a large number of required tests need to be carried out to screen for the potential ranges where the composite tubes may be susceptible to SCC in wash waters at lower temperatures. Tests planned under ORNL-funded program are expected to finish by September 1998.

Table IV. Results from 304L specimens tested in different environments using slow strain rate of $2x10^{-6}/s$

SP#	Test Solution	Temp. °C	E, mv (SCE)	Remarks
3	(1N)Na_2S $9H_2O$	90	OCP	No Crack
4	(1N)Na_2S $9H_2O$	25	OCP	No Crack
5	(1N)Na_2S $9H_2O$ +Na2CO3	90	OCP	No Crack
6	(1N)Na_2S $9H_2O$ +Na2CO3	25	OCP	No Crack
7	(1N)Na_2S $9H_2O$	25	OCP	No Crack
8	(1N)Na_2S $9H_2O$	102	OCP	No Crack
13	Artificial WW# 1	90	OCP	No Crack
14	Artificial WW # 1	200	OCP	Multiple SCC Cracks
15	Artificial WW # 2	90	OCP	No Crack
16	Artificial WW # 1	150	OCP	No Crack
17	Crystals of Na2S and H2O	100	OCP	No Crack
19	150 gm Na_2S+150 gm NaOH +50 ml H2O	100	OCP	Multiple SCC Cracks
20	Artificial WW # 1	200	OCP	Multiple SCC Cracks
21	NaOH=300 gms., H2O=50ml	100	OCP	No Crack
22	Artificial WW # 1	200/90	OCP	No Crack
23	Na2S=150,NaoH=150,H2O=50ml	100 C	OCP	No Crack
24	Artificial WW # 1	200/150	OCP	Multiple SCC Cracks
25	Artificial WW # 1	100 C	-0.740	No Crack
26	Artificial WW # 3	200C	OCP	Multiple SCC Cracks
27	Artificial WW # 3	100 C	-0.740	No Crack
28	Artificial WW # 3	100 C	-0.650	No Crack
29	Artificial WW # 1	100 C	-0.650	No Crack
30	Artificial WW # 3	200C	OCP	Multiple SCC Cracks

CORROSION IN CLOSED CYCLE MILLS

PROJECT F019

ANNUAL RESEARCH REVIEW

March 26, 1997

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Confidential Information - Not for Public Disclosure
(For IPST Member Company's Internal Use Only)

TECHNICAL PROGRAM REVIEW

Project Title: CORROSION IN CLOSED CYCLE MILLS
Project Number: F019
Division: Chemical and Biological Sciences
Project Staff: P. Singh, G. Fonder, S. Stalder, D. Silimon
FY 97-98 Budget: $119,079

PROGRAM OBJECTIVES:

To identify key corrosion and materials-related issues, which may impact the successful implementation of various closed mill scenarios and provide support to maximize the potential of these new technologies.

SUMMARY OF RESULTS:

Design of mill closure, equipment materials used, corrosion related problems, and general effects of water closure in the paper machine area and the bleach plant/pulp mill areas are different. Even though, some of the mills may opt to use water from some pulp mill stream in paper machine area or *vice versa,* but to handle this broad topic effectively the project was divided into two categories.

1. **Task 1 Effects of white water closure on corrosion of the paper machine**
2. **Task 2 Effects of bleach plant closure on corrosion of the existing equipment**

On PAC's recommendations we started working on Task 1 of this project. This task was started with the literature search to understand different mill closure designs, which the pulp and paper industry has adopted or may adopt in the future. It must be realized that this topic is very broad and needs very thorough understanding of various interdisciplinary areas. One needs to know about the proposed changes in the process, their effects on the local chemical environments, material used for the equipment, chemical composition of the material used, manufacturing history and resultant microstructure of the material, effects of the local environment on a particular microstructure. Unfortunately, important information in some of these areas is lacking. Simple questions like, " what are chemical changes in local streams ?" are not clear. Modeling work is going-on at IPST and other research organizations which will be very important for our objective of being able to predict corrosion behavior of the equipment.

Literature review was conducted with main objective to understand the effects of different environmental parameters on corrosion of the existing equipment. Based on this knowledge, we have started an experimental program to map-out limits of a given material to environmental changes. Summary of the literature search is included in this report and the draft of the literature review paper is in preparation.

Cyclic polarization tests were conducted to study the corrosion behavior of six different materials, representing three commonly used materials and three relatively new materials. Five different white water compositions, corresponding to different mill closure scenarios, were used in these tests. Coupon exposure tests will also be done on these materials to confirm our observations from the electrochemical tests. This set of proposed tests is expected to finish by the end of September 1998.

Progress of this project is slower than our expectations as there was lack of the manpower in the beginning of this project. In last four months, Corrosion and materials group at IPST has grown to a level where we will be able to carry out this project well. However, we have made some progress to start an experimental program for this task. Results from these experiments are discussed in the following sections.

Task 1 Effects of white water closure on corrosion of the paper machine

Summary of Literature Review:

Many relevant papers on the effects of white water closure on paper machine corrosion were identified and collected. These publications are listed at the end of this report[1-70]. The list is not complete by any means; however, these papers address some of the major concerns in this field. A number of papers in this list[1-3, 5, 20, 25, 26, 30, 33, 39, 41, 43, 48, 53] discuss various white water closure designs and their effects on the environmental changes in this system. There are different designs of paper mill closure as well as different degrees of water reuse. Even though there are similarities in the overall philosophy of the mill closure but, the changes in the closure design may have significant effects on the resulting local environments and their corrosivity. Local environments, that any given equipment may get exposed to, may also vary from mill to mill.

Papers collected so far can be divided into six major categories:

1) Papers related to the *white water closure design* with speculations on the effects of the resultant environments on corrosion.[12, 15, 22, 24, 29, 40, 42, 46].

2) Papers based on the *mill survey* on the corrosion in closed mills.[20, 26, 37, 43, 47, 70]

3) Papers with *field results* on corrosion in the closed white water systems. [6, 8, 9, 11, 13, 14, 17, 27, 37, 38, 44, 49-52]

4) Papers which discuss *laboratory tests* in the simulated white water environments. [10, 32, 44]

5) Papers on material selection and other proposed *corrosion mitigation schemes* for the closed paper mills.[4, 21, 23, 24, 31, 34]

6) *Microbial corrosion* problems in the closed white water systems.[9, 44-46, 49-51]

The general theme of the papers, which reported survey results from the paper mills with various degrees of closure, was that the closure resulted in an increased corrosion in these mills.[26, 37, 43, 47]

Some of the papers in this list have discussed various material selection related issues as well as chemical control methods for the closed white water systems to mitigate corrosion [4, 15, 21, 23, 24, 31, 34]. Papers which deal with chemical control methods generally address microbial corrosion problems in the white water systems and have discussed the use of various biocides to fight the microbial activity in closed white waters[9, 44-46]. There is also some concern about the increased concentrations of felt cleaning agents in the closed system and their adverse effects on corrosion in paper machines[23]. Roll manufacturers are concerned about the anticipated corrosion problems due to decreased pH, increased chloride levels, higher temperatures, and increased organic activities in the white water systems[34].

An experimental study[32] conducted to simulate a particular design of white water closure has shown that the uniform corrosion rates of 304-L stainless steels were not significantly increased in recycled white water; however, the other forms of corrosion such as pitting corrosion and stress corrosion cracking susceptibilities of 304-L increased considerably.

IMPACT OF WHITE WATER CLOSURE ON CORROSION

White water closure is expected to result in certain environmental changes in the mill process streams. However, that does not mean that there will always be more corrosion in the closed mill environments. Corrosion of the mill equipment due to mill closure is not only dependent upon the environmental changes but is also dependent upon the type of materials used for construction.

Environmental changes expected in different areas of pulp and paper mills are different. This literature review is done to address a mill closure from the point of view of changes in the white water environment and will not discuss any specific material of construction in detail. One reason for this approach is that if we know the environmental changes in closed systems then we can select an appropriate material. There are commercially available materials for almost all anticipated closed mill environments and some of these materials are already being used successfully in other process industries with similar environments. However, use of some of these new materials may require more capital.

Mills, which are modifying their equipment for closure, or are installing new equipment have an opportunity to select corrosion-resistant materials for the anticipated environment. Whereas, for other mills which decide to use its existing equipment in the closed white water environment, the corrosion concerns may need to be evaluated very carefully. In either case, to evaluate and predict corrosion of the paper machine equipment in the closed white water, one needs to have sound understanding of the environment and specific corrosion problems of that mill before the closure is introduced. Then the anticipated changes in the local environment can be used to predict the corrosion behavior of given materials after the closure is introduced. Corrosion prediction can either be based on some laboratory testing in the anticipated environments or can be based on the published literature (if available). We have extracted some of the published data on white water compositions and the corresponding corrosion behavior of some of the materials tested. Results are listed in Table VI. Although, some of the expected trends like increase in corrosion with decrease in pH and increase in chloride levels is reflected in some of this data but the correlation of the chemical composition of white water and corrosion of different materials is not very clear from this table with very limited data. However, We will continue to extract similar data from other published sources and old PAC reports with an aim to deduce some clear trends on the white water chemistry and its effects on the corrosion of different materials.

CLOSURE OF THE WHITE WATER SYSTEM

Unexpected corrosion due to white water closure may result in unscheduled downtime. Machine operators need to know what the current status of their paper machines is regarding white water corrosivity and materials used, and what new corrosion problems may arise due to white water closure. Some of the expected environmental changes and their effects on the corrosion can be summarized as following:

- Closure of white water systems is expected to result in increased concentrations of some important anions like Cl^- and $S_2O_3^{-2}$.
- Other expected changes include increase in temperature, high levels of dissolved and colloidal chemical species, high levels of residual brightening agents, and higher microbial activity.
- The extent of these changes will strongly depend upon the design of closure loops.
- Corrosion of the equipment in the paper machine area depends upon changes in the environment as well as on the materials used for equipment construction.

Organization chart, shown in Figure 21, schematically shows how various closure variables need to be considered before we can answer a simple sounding question," What happens to the paper machine equipment when we close white water system ?". To address this question effectively, we are trying to collect all available published field data at one place and analyze it. This effort should be run in-parallel with the on-going experimental program where we can test these effects in a controlled manner.

There is some concern over the increase in sulfate levels in the white waters, above 3 g/l, which may deteriorate the reinforced concrete installations in effluent purification systems. Although this does not fall into metal corrosion category, but for the structural integrity of the paper machine equipment, this may be of prime importance and needs to be further investigated. Use of polymer coating is one of the practical ways to prevent this effect. However, other alternatives need to be looked at.

Factors Affecting White Water Corrosivity

Main factors effecting white water corrosivity are chemical composition, pH, and water conductivity for the materials such as cast iron and copper based alloys[14, 52, 24]. Concentrations of inorganic species in the white water depends on the type of wood pulped, fresh water source, pulping processes, bleaching processes, and the paper machine wet end chemistry.

Corrosion of stainless steel and other materials critically depends on the various ionic species present in the water. To predict the corrosion of the paper machine area, it is important to understand the effect of each chemical constituent on the corrosivity of white water.

Thiosulfate ($S_2O_3^{-2}$).

Thiosulfate ions in white water can cause pitting in 304 and CA15 stainless steels[24, 48]. The presence of critical concentrations of thiosulfate ions in white water lowers the pitting potential of 304 stainless steels as the thiosulfate enters the pits and stimulates their growth. However, at higher potentials, the pits repassivate because thiosulfate can no longer be reduced to an activating adsorbed species [24, 48]. Sensitized 304 can undergo pitting in the range 3 to 75 ppm of $S_2O_3^{-2}$. Thiosulfate ions also increase the propagation rate of the crevice corrosion in 304 and 316 stainless steels in concentrated (1M) NaCl. It was reported that thiosulfate did not have any effect in the situations where the chloride solutions were incapable of initiating crevice corrosion attack.

Chlorides and Sulfates (Cl^-, SO_4^{-2}).

For 304 stainless steel, the presence of sulfate makes the formation of stable pits more difficult; for the $[SO_4^{-2}]/[Cl^-]$ molar ratio approaching 1, the breakdown potential rises with an increase in SO_4^{-2} ion concentration, which means that the pitting becomes more difficult. Bower[14-16],Wensley[52], and Bennett and Federowicz[8] independently have shown through electrochemical tests that the higher concentrations of sulfate are beneficial as it raises the breakdown potential and therefore helps in localized corrosion initiation.

Various authors including Bowers[14-16] and Wensley[52] have used some empirically derived ratios of different constituents of white water to explain corrosion behavior of these environments. The severity of pitting has been related to the ratio $\frac{[SO_4^{-2}]+[Cl^-]}{[S_2O_3^{-2}]}$.

For 304 stainless steel in the presence of thiosulfate, the inhibiting effect of sulfate is related to the electrochemical reduction of the $S_2O_3^{-2}$. 316 stainless behaves in a similar fashion to the 304 stainless steel in the absence of $S_2O_3^{-2}$ ions. However the breakdown potential for 316 stainless steel is higher than the 304 stainless steel. Above 60°C, thiosulfate can accelerate pitting attack on 316 stainless steels.

Thiosulfate does not affect the pitting behavior of 316 stainless steels unless the Cl^- concentrations are above 1000 ppm and SO_4^{-2} ion concentration is negligible [24, 48]. 304 stainless steels can undergo stress corrosion cracking in chloride-containing media above 60°C. Cracking of 304 steel has been reported in solution with 1500 ppm Cl^- at 100°C. Temperatures are not expected to rise above 60°C in most of the white water system. If the white water with a higher chloride concentration is used in some other part of the mill where the temperatures are higher, such as chip refiners, then stress corrosion cracking problems may arise in the refiner areas.

<u>Sulfite and Bisulfite Ions (SO_3^{-2}, HSO_3^{-2}).</u>

The pitting tendency of 304 stainless steels also depends upon [SO_3^{-2}] and [HSO_3^{-2}]. It has been reported that the maximum pitting of 304 stainless steel occurs when the ratio $\frac{[SO_4^{-2}]+[Cl^-]}{[S_2O_3^{-2}]}$ was between 10 and 30 and the [SO_4^{-2}] + [Cl^-] > 0.2 [SO_3^{-2}]. Bisulfite ions inhibit pitting of 304 stainless steels in white water systems. Pitting is fully inhibited when [HSO_3^{-2}] > [SO_4^{-2}]. However, the beneficial effects are seen above bisulfite concentrations of about 0.2 [SO_4^{-2}] ion concentrations in white waters. A similar effect is expected if the [HSO_3^{-2}] ion concentration in the white water is more than the [Cl^-] ion concentration.

<u>Hydrogen Peroxide (H_2O_2).</u>

Hydrogen peroxide is generally not present in white water systems. In mills where hydrogen peroxide bleached pulp is used, there are chances that some residual hydrogen peroxide which is not removed by SO_2 souring may enter the paper machine.
Residual of 60 ppm or more has been reported in machine white waters at an acid pH [24, 48]. The major effect of the residual hydrogen peroxide is copper alloy suction rolls. Increased corrosion of CDA 360 brass, de-alloying of NiAl bronze, and higher corrosion rates of martensitic stainless steels compared to the 304 stainless steel are some of the reported effects of residual hydrogen peroxide in white water systems.

Dissolved and Colloidal Material

These materials originate from wood, comprising carbohydrates, liginin, extractives, and ash. They do not participate directly in the corrosion of equipment in white water systems but can enhance bacterial activity and slime formation. Bowers [14] reported that the corrosion of carbon steel decreased at > 10,000 ppm of (10 gL^{-1}) dissolved solids, due to a film (scale) buildup.

Microbial Corrosion

Many authors have reported that microbial activity increases due to white water closure[9, 44-46, 49-51]. Colonies of the sulfate reducing anaerobic bacteria on the equipment surface cause localized corrosion attack under these colonies. Carbon steel as well as stainless steel are attacked by this mode of corrosion. Increased temperatures above 60°C may help in eliminating some of the sulfate reducing bacteria strains from a closed white water system. Continuous cleaning and sterilizing treatments are required before these colonies are established to avoid this type of corrosion problem.

The impact if reduced effluent operation will also effect the process control in mill operations. A small process upset in one area may have a larger impact on the equipment in other areas of the closed mill. Material selection should not only be based on everyday process parameters and resultant environments, but should also consider potential upsets in the mill. This means that some of the marginal materials like carbon steel may become unacceptable under that approach. These uncertainties make the material selection, and corrosion prediction of the equipment in closed mills a challenging task. Mill engineers will have to develop a sophisticated approach to mitigate corrosion by material selection, corrosion prevention technology, and appropriate closed mill designs.

Some of the areas of concern along with the known reasons for corrosion in the white water system are listed by Garner and Thompson [24, 48] and are summarized here.

<u>Suction rolls.</u>

- If thiosulfate and other reduced sulfur compound concentrations increase, then the bronze rolls may have higher corrosion rates.
- Modern duplex or precipitation hardened stainless steels are not expected to have major problems in closed white waters, although some alloys (i.e., Alloy 75, VKA 171) can undergo thiosulfate-induced pitting.

The effects of residual peroxide in a white water system need further investigations. Corrosion fatigue of roll journals may also become an increasing problem due to higher concentrations of chlorides in white water.

Carbon steel and cast iron structures.

- Increased temperature, chloride ion concentrations, conductivity, and velocity would increase the carbon steel corrosion rate. Therefore, increases in temperature, chloride concentration and conductivity due to mill closure may result in higher corrosion rates for carbon steel and cast iron structures in white water systems.

Austenitic stainless steel structures.

- Sensitized 304 stainless steel would fail rapidly in closed water systems.
- Increased concentrations of chlorides, sulfates, and thiosulfates, as well as increases in temperature due to mill closure, will increase localized corrosion of 304L stainless steels depending upon ionic ratios.
- Residual peroxides in white water would assist chloride-induced corrosion, but reduce the effect of thiosulfate by direct reaction with it.
- Increased microbial activity may increase the probability of localized corrosion in closed white waters.
- 316L stainless steel performs very well in present white water systems. However, if the $[SO_4^{-2}]/[Cl^-]$ molar ratio is less than 1, then 316L may be subjected to pitting attack due to thiosulfates in the white water.

Wet end framework.

- Generally the framework is either constructed or is protected by 304 or 316 stainless steel layer.
- Pitting is possible in situations where ClO_2 is carried over into the white water from the bleach plants.
- Sensitized austenitic stainless steels may undergo stress corrosion cracking.
- Closure may promote the above stated corrosion attacks due to an increase in temperature and chloride ion concentrations in the white water system.

Possible Effects of White Water Closure on Corrosion

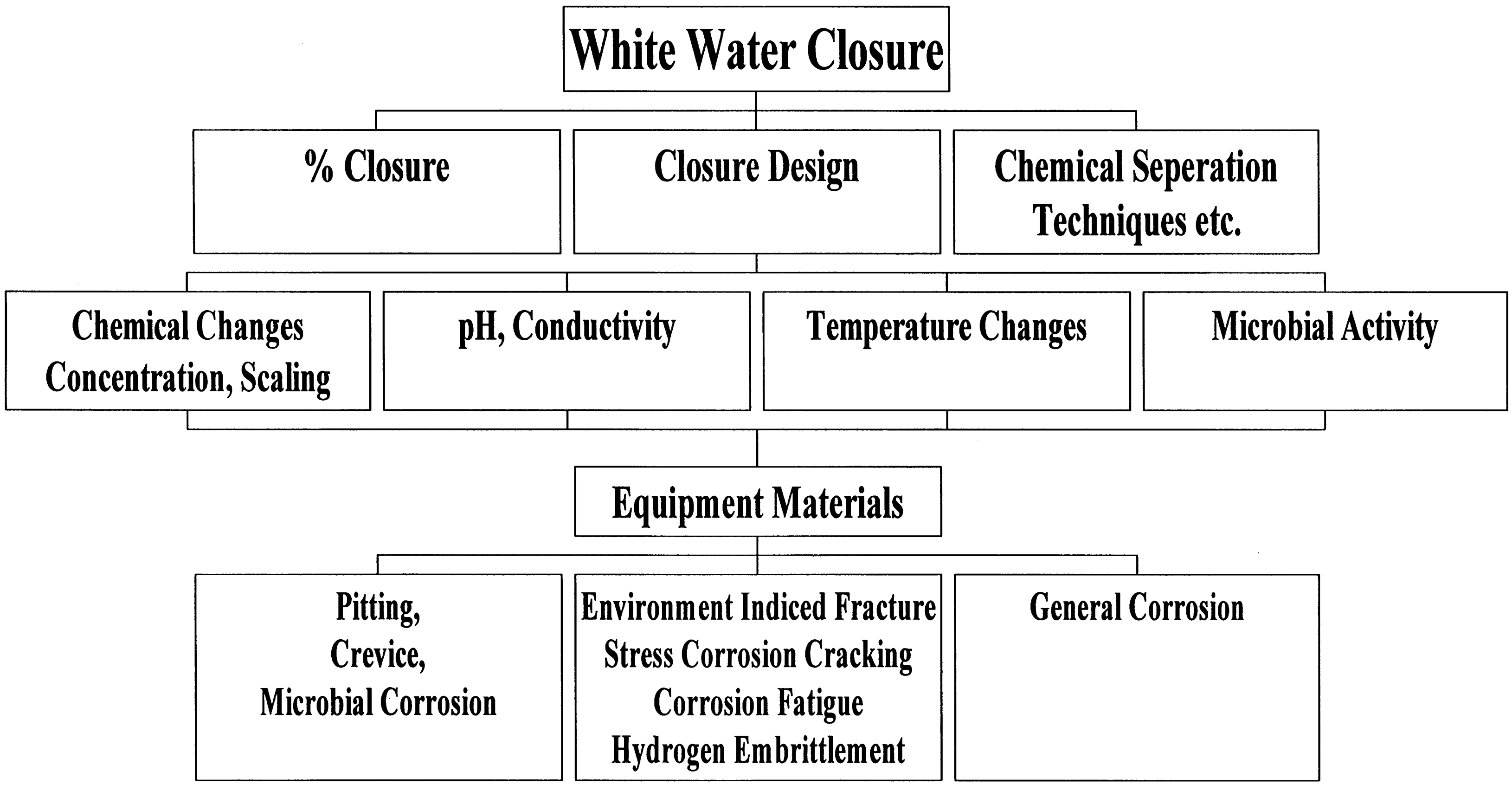

Figure 21. Organization chart showing how the corrosion of any given material will

Experimental Program:

Experiments for this project were designed to study the effects of white water closure on the materials, commonly used in the paper machine areas, as well as some alloys which are less common but are resistant to corrosion in similar environments. Two type of laboratory tests are planned for this project; cyclic polarization tests, and coupon exposure tests in different white water solutions.

Cyclic polarization experiments were carried out in simulated white water environments, representing different scenarios of paper mill closure. Table V shows the test matrix of different white water compositions tested so far in this project. The white water compositions, tested so far, were chosen with an objective of determining the concentration limits, of each of the white water constituents, that can be safely handled by a given material.

Cyclic Polarization Tests:

Baseline solution was same as the TAPPI- D solution used in some of the previous studies, whereas, the "strong solution" represent a scenario where the white water concentrates in local areas and the concentration of all constituents increase by 10 factor of 10. Other two solutions tested represent different scenarios where either the chloride ion concentration is high, " high-Cl solution", or where sulfate ion concentration is higher, " high-sulfate solution", than the baseline solution. Last solution tested in this study did not have any thiosulfate ions but rest of constituents were similar to the baseline solution. All tests were conducted at 50°C and the pH of all solutions was adjusted to 4.0. Test solutions were made fresh everyday to avoid any changes in the composition with time.

Six different materials were tested in each solution and these are 1018 carbon steel, 304L, 316L, 317L, 2205 and SMO254. These materials cover some of the commonly used material as well as some candidate materials like SMO254 and 2205 duplex stainless steel which have good corrosion resistance to this type of environments.

Potential scan rate for all of the results shown here was 0.2mv/sec. We did some tests at higher scan rates to compare them with the slow scan rate curves to get some idea of the stress corrosion cracking susceptibilities. Fast scan rate test are not complete yet. Results from the cyclic polarization tests are shown in Figures 22 to 31. Figures 22 and 23 show cyclic polarization results for the baseline solution. All stainless steels tested in baseline solution had comparable behavior in terms of the open circuit potential, passivation current density as well as breakdown potential except for the SMO254 SS, which had lower passivation current density than the rest of the steels tested. This indicates that 304L and 316L behave similar to the higher grade materials with higher Mo content. Similarly, results from the "high-Cl solution, shown in Figures 24 and 25, show similar trend that different grads of stainless steel behave in very similar fashion during the forward scan. However, during the reverse scan, 304L, 316L, and 317L show signs of susceptibility to localized corrosion as the current did not decrease with the decrease in the potential. These test are being repeated to check this behavior. Coupon tests will also be done to confirm these results.

Polarization scan from the "strong solution" show that 2205 duplex stainless steel and SMO254 had lower passivation current densities compared to 304L, 316L as well as 317L stainless steel. Results from "high sulfate solution" are shown in Figures 28 and 29. Bowers(14-16),Wensley(52), and Bennett and Federowicz(8) have shown that the higher concentrations of sulfate is beneficial in typical white waters as it raises the breakdown potential and therefore helps in localized corrosion initiation. Our results have not shown this effect conclusively but the sulfate concentrations in present set of tests are probably not high enough to see these effects. We will repeat these tests and will also carry out some tests at higher levels of sulfate to check its effects.

Tests were also done on c-steel which have shown very high corrosion rates even in baseline solution, as calculated from Tafel slopes. The corrosion rates increased considerably in the high-Cl solution as well as strong solution. This reinforces conventional knowledge that the structural frame etc. made out of carbon steel in wet white water area need to be protected by barrier coatings. This is even more important in the closed white water systems where the white water will be more aggressive for the carbon steels.

We are repeating some of the cyclic polarization tests to check their reproducibility. These preliminary set of results indicate that only in the strong solution and high chloride situations, higher grades of stainless steel like SMO254, 2205, have clearly higher resistance in terms of lower passivation current density and resistance to the localized corrosion. These results will be confirmed by coupon tests where multiple coupons will be exposed to different test solutions and their behavior in terms of general corrosion and localized corrosion will be monitored. We expect to finish these test by September 1998.

PROJECT GOALS: (until October 98)

1) To write a review paper on the literature on white water closure and its effects on corrosion and send it to PAC members for their review.
2) Finish coupon exposure tests in the test solutions described in this report.
3) Continue an experimental program based on PAC-98 meeting discussions and PAC's recommendations to test selected materials in the simulated close-white water environments and map out their performance limits.

GOALS FOR FY 98-99

1) Complete the final version of the review paper on effects of closure in white water systems.
2) Continue with experimental test program in closed white water systems after including PAC's recommendations.
3) Start with the literature review on effects of closure on corrosion in the pulp mill / bleach plant area. and design a test program to study these effects.

Table V. Simulated White Water Solutions Compositions Used for Potentiodynamic Polarization Tests

Environment	Cl^- ppm	SO_4^{-2} ppm	$S_2O_3^{-2}$ ppm	pH	Temp. °C
Base Line (TAPPI -D)	200	500	50	4.0	50
High-Cl Solution	1000	500	50	4.0	50
High-Sulfate Solution	200	2500	50	4.0	50
Strong Solution	2000	5000	500	4.0	50
No-Thio Solution	200	500		4.0	50

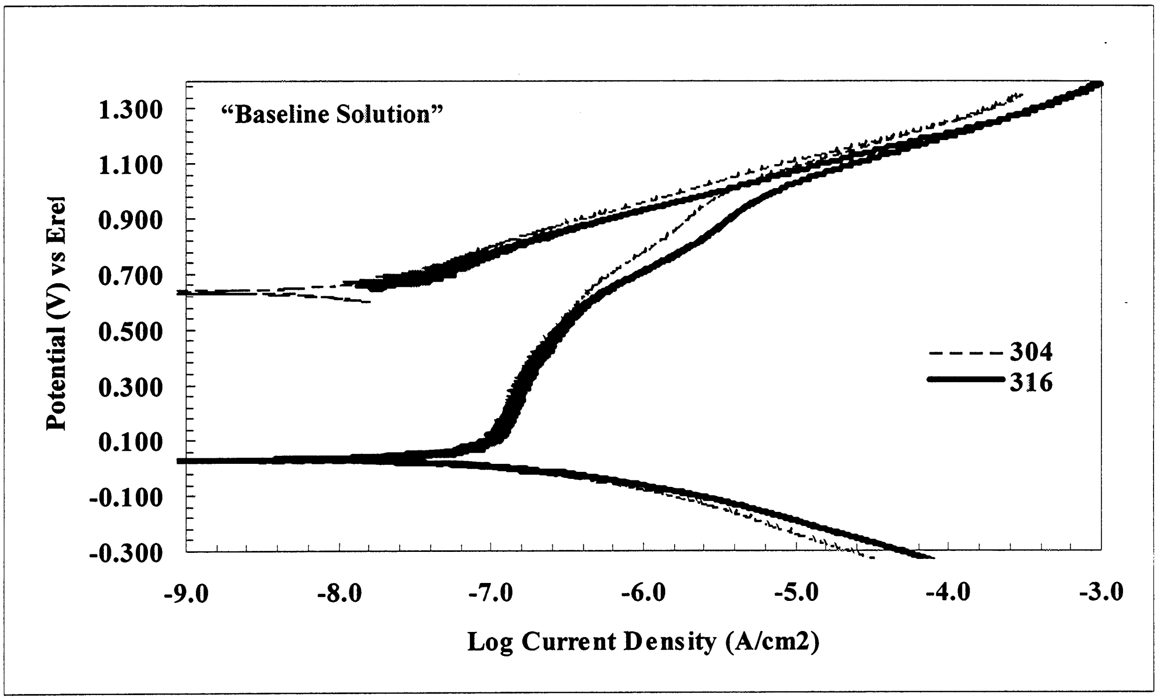

Figure 22 Cyclic polarization curves for the materials tested in "Baseline Solution" at 50°C at a scan rate of 0.2 mv/sec.

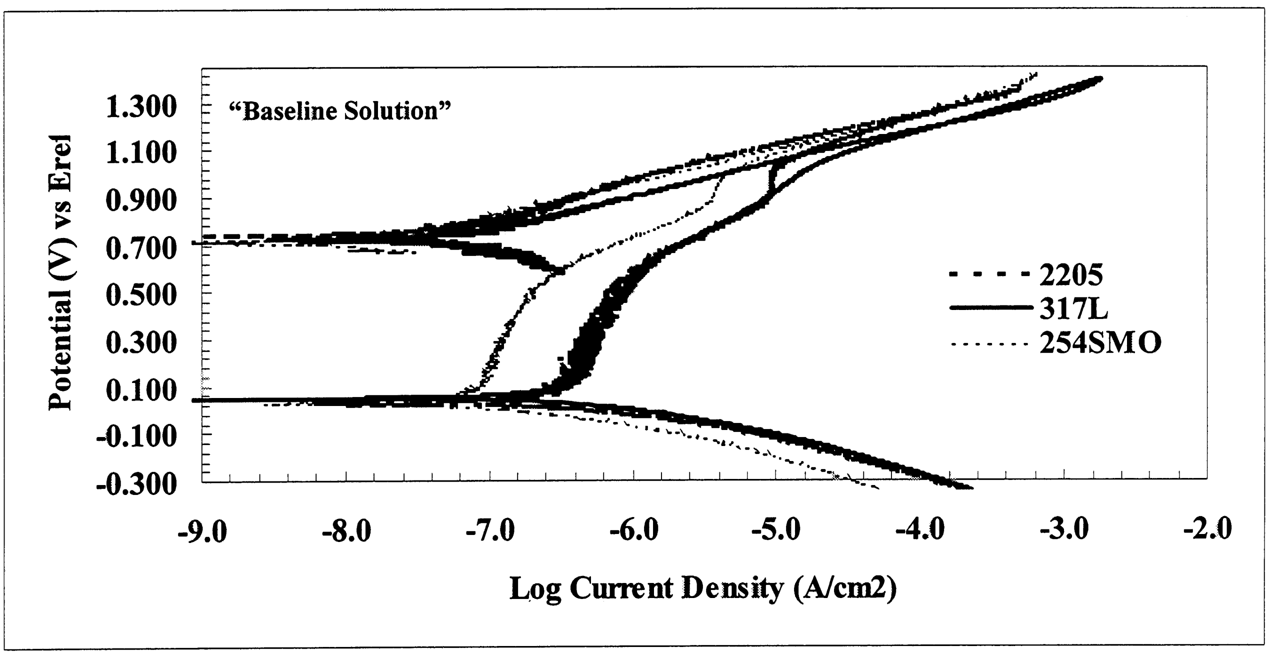

Figure 23 Cyclic polarization curves for the materials tested in "Baseline Solution" at 50°C at a scan rate of 0.2 mv/sec.

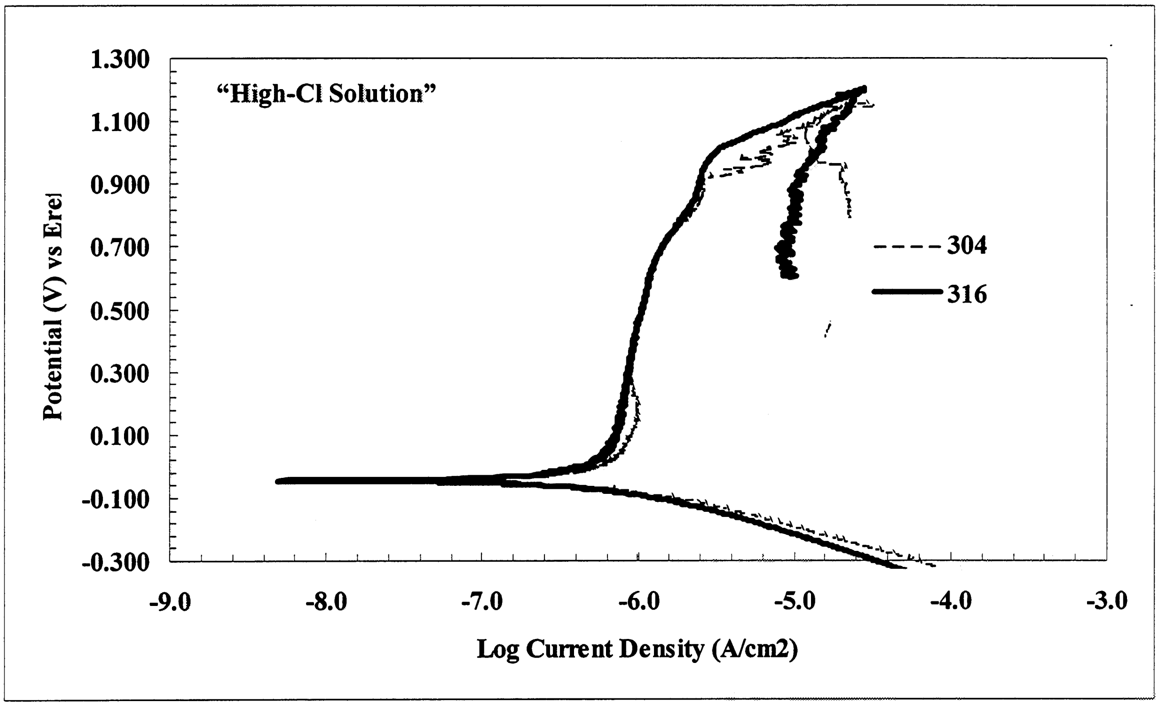

Figure 24 Cyclic polarization curves for the materials tested in "High-Cl solution" at 50°C at a scan rate of 0.2 mv/sec.

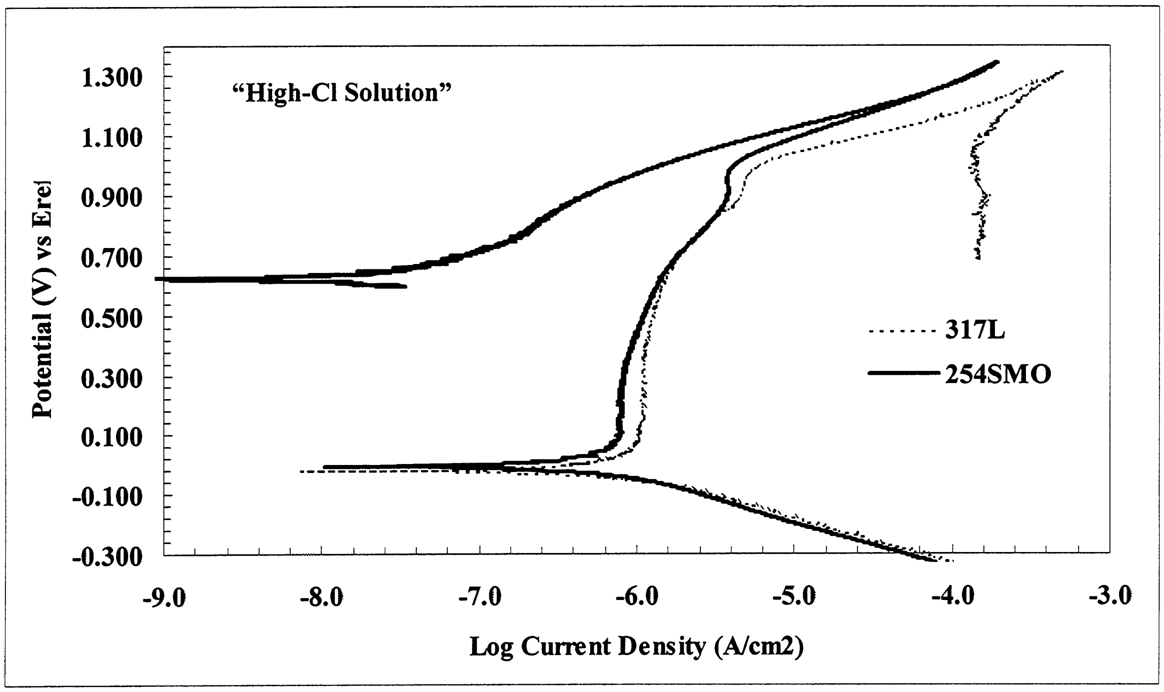

Figure 25 Cyclic polarization curves for the materials tested in "High-Cl Solution" at 50°C at a scan rate of 0.2 mv/sec.

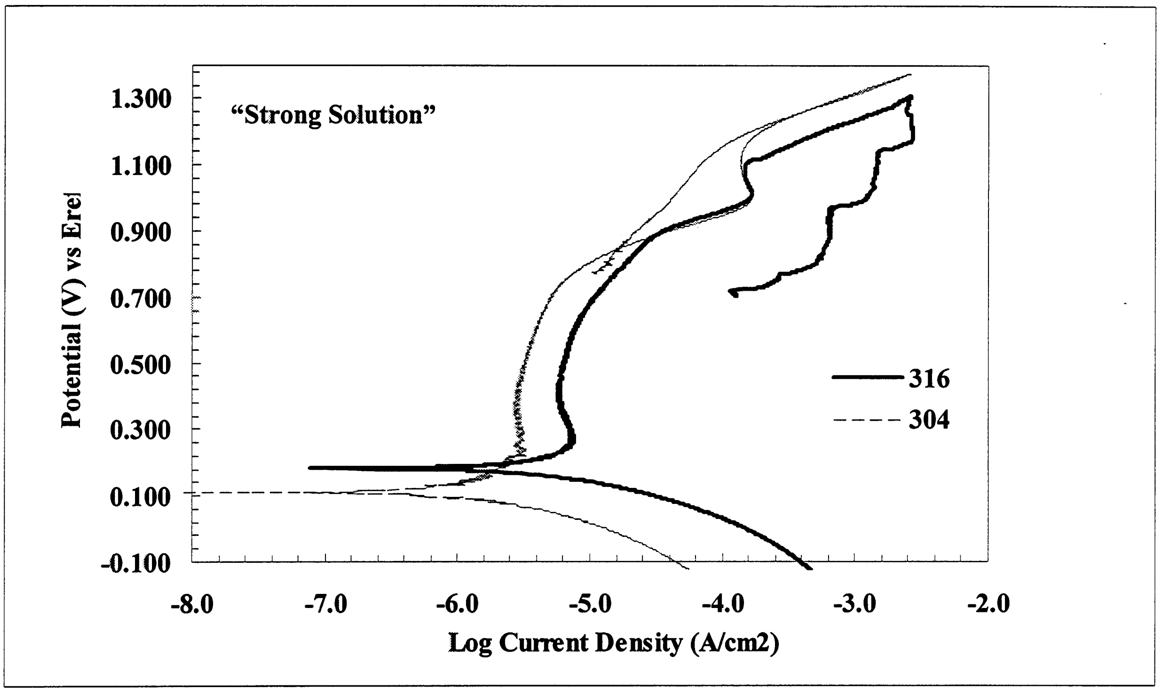

Figure 26 Cyclic polarization curves for the materials tested in "Strong Solution" at 50°C at a scan rate of 0.2 mv/sec.

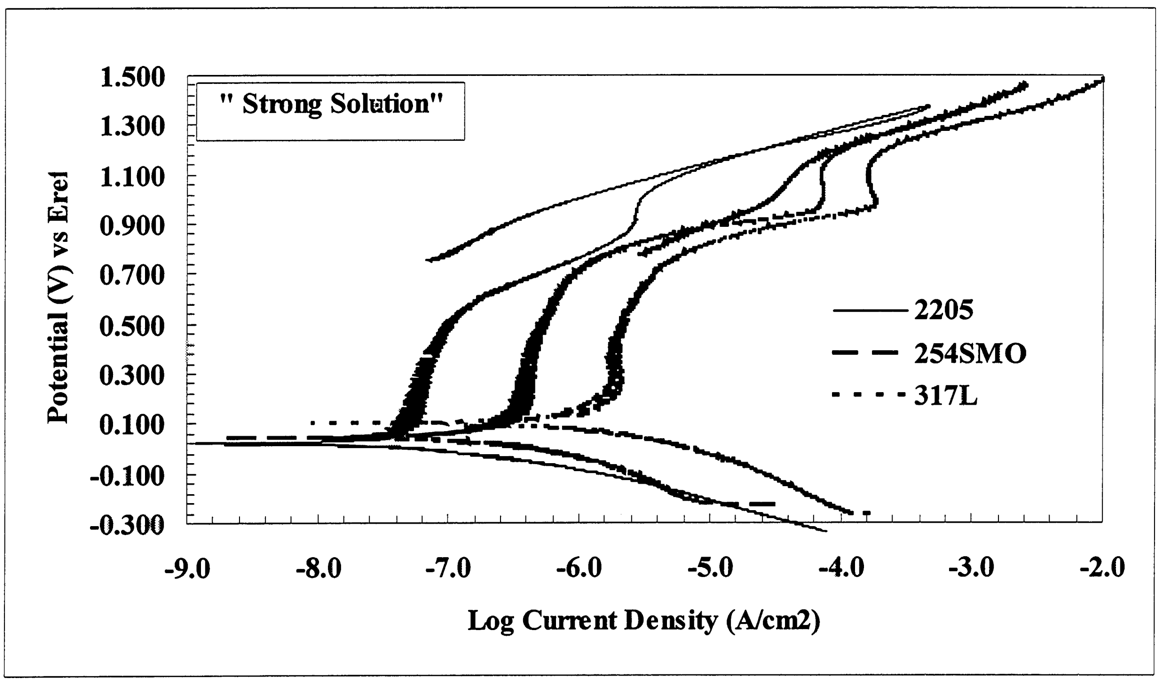

Figure 27 Cyclic polarization curves for the materials tested in "Strong Solution" at 50°C at a scan rate of 0.2 mv/sec.

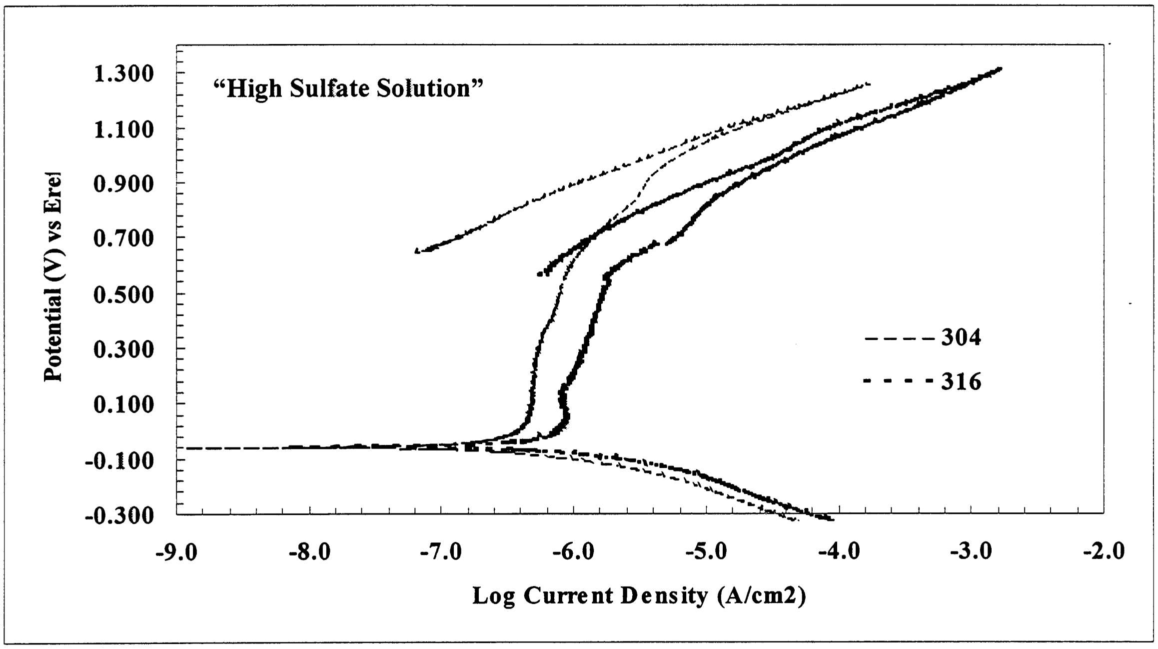

Figure 28. Cyclic polarization curves for the materials tested in "High Sulfate Solution" at 50°C at a scan rate of 0.2 mv/sec.

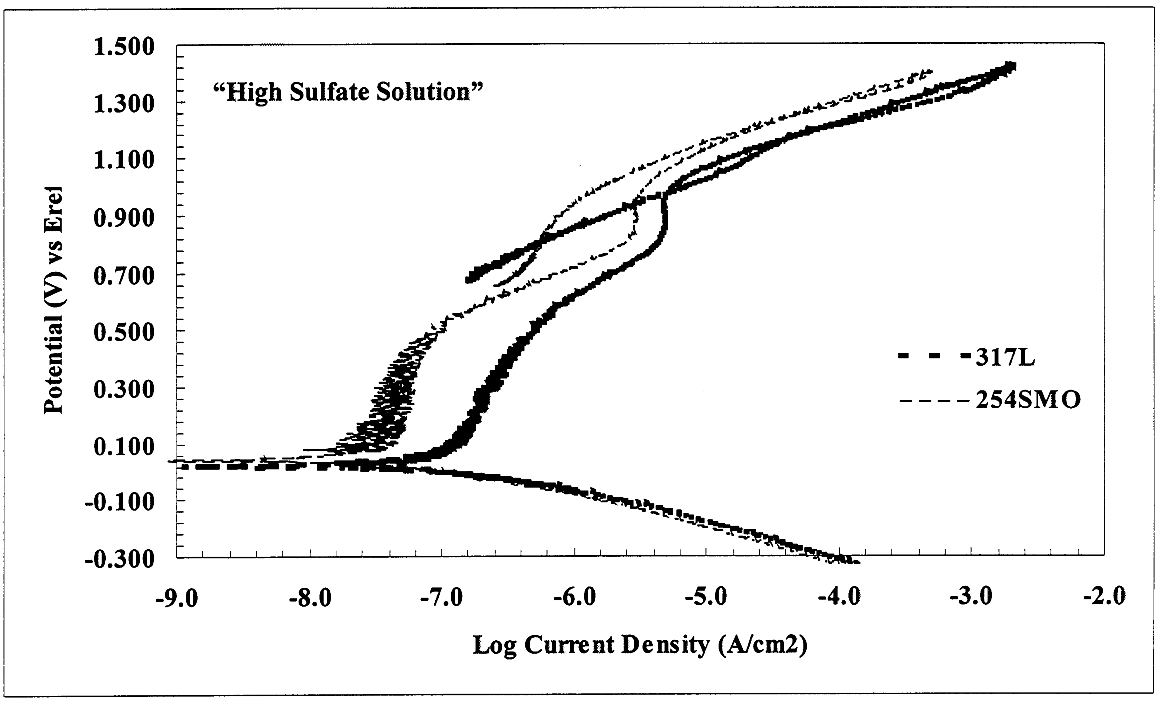

Figure 29. Cyclic polarization curves for the materials tested in "High Sulfate Solution" at 50°C at a scan rate of 0.2 mv/sec.

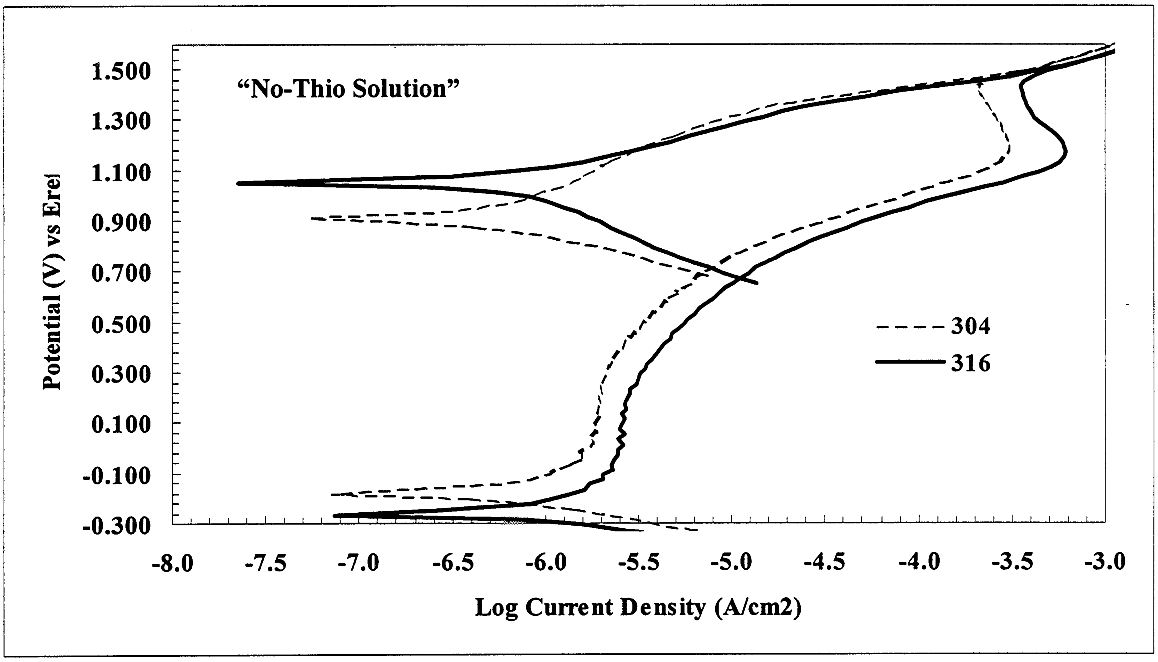

Figure 30. Cyclic polarization curves for the materials tested in "No-Thio Solution" at 50°C at a scan rate of 0.2 mv/sec.

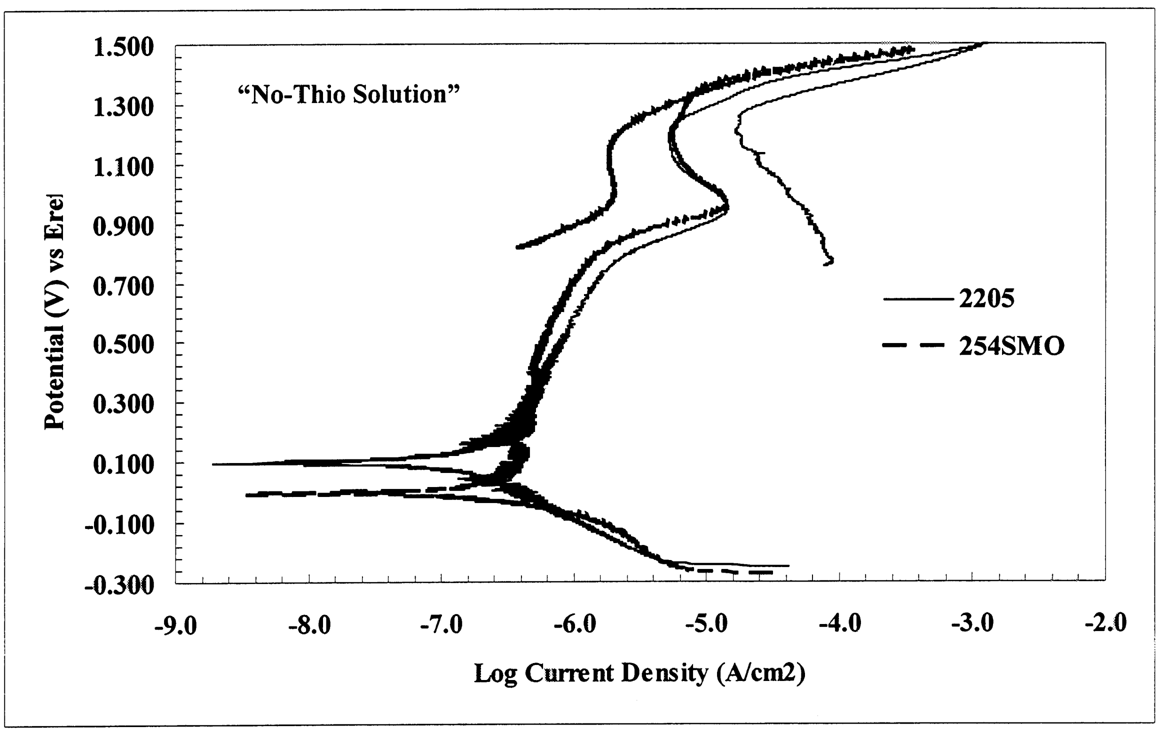

Figure 31. Cyclic polarization curves for the materials tested in "No-Thio Solution" at 50°C at a scan rate of 0.2 mv/sec.

Table VI. Published Data on Corrosion in Different White Water Compositions

				White Water Corrosion Data								
lant Area	Material	Corrosion Type	Corr. Rate	White Water Source	Cl^-	SO_4^{-2}	$S_2O_3^{-2}$	Ca^{+2}	Temp.	pH	Conductivity	Ref.#
Clarified H2O	304 SS	pitting, crevice	"moderate"	real white water	76 mg/L	65 mg/L			no data	7.3	597 mohms/cm	17
	304 SS	pitting, crevice	8 mpy	real white water	76 mg/L	460 mg/L			100 F	7	1520 mohm/cm	17
	304 SS	pitting, crevice	4 mpy	real white water	50 mg/L	195 mg/L			97 F	5.9	2770 mohm/cm	17
	304 SS	pitting, crevice	70 mpy	real white water	100 mg/L	235 mg/L			96 F	5	2770 mohm/cm	17
	304 SS	pitting, crevice	15 mpy	real white water	185 mg/L	267 mg/L			94 F	6.3	4270 mohm/cm	17
Linear H2O	304 SS	pitting, crevice	"moderate"	real white water	86 mg/L	63 mg/L			no data	7	703 mohm/cm	17
	304 SS	pitting, crevice	10 mpy	real white water	76 mg/L	600 mg/L			100 F	6.8	1480 mohm/cm	17
	304 SS	pitting, crevice	90 mpy	real white water	100 mg/L	251 mg/L			102 F	5	2830 mohm/cm	17
	304 SS	pitting, crevice	45 mpy	real white water	205 mg/L	321 mg/L			100 F	6.6	4460 mohm/cm	17
Filler H2O	304 SS	pitting, crevice	"moderate"	real white water	74 mg/L	64 mg/L			no data	7.1	673 mohm/cm	17
	304 SS	pitting, crevice	20 mpy	real white water	118 mg/L	680 mg/L			110 F	6.5	1560 mohm/cm	17
	304 SS	pitting, crevice	3 mpy	real white water	20 mg/L	142 mg/L			99 F	6.5	2970 mohm/cm	17
	304 SS	pitting, crevice	55 mpy	real white water	103 mg/L	267 mg/L			103 F	5.1	2940 mohm/cm	17
	304 SS	pitting, crevice	12 mpy	real white water	198 mg/L	325 mg/L			98 F	6.5	4450 mohm/cm	17
N/A	mild steel	uniform	60 mpy	simulated white water	200-500 ppm				amb	6		16
	mild steel	uniform	80 mpy	simulated white water	200-500 ppm				amb	7		16
	mild steel	uniform	63 mpy	simulated white water	200-500 ppm				amb	8.5		16
	mild steel	uniform	19 mpy	simulated white water	200-500 ppm				amb	9.7		16
	mild steel	uniform	18 mpy	simulated white water	200-500 ppm				amb	10		16
	mild steel	uniform	15 mpy	simulated white water	200-500 ppm				amb	11		16
	mild steel	uniform	15 mpy	simulated white water	200-500 ppm				amb	11.6		16
	mild steel	uniform	15 mpy	simulated white water	200-500 ppm				amb	13		16
	mild steel	uniform	87 mpy	simulated white water	1000 ppm				amb	6		16
	mild steel	uniform	113 mpy	simulated white water	1000 ppm				amb	7		16
	mild steel	uniform	118 mpy	simulated white water	1000 ppm				amb	8.6		16
	mild steel	uniform	35 mpy	simulated white water	1000 ppm				amb	10		16
	mild steel	uniform	22 mpy	simulated white water	1000 ppm				amb	11		16

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	mild steel	uniform	20 mpy	simulated white water	1000 ppm				amb	11.6		16
	mild steel	uniform	20 mpy	simulated white water	1000 ppm				amb	13		16
	mild steel	uniform	132 mpy	simulated white water	4000 ppm				amb	6		16
	mild steel	uniform	132 mpy	simulated white water	4000 ppm				amb	7		16
	mild steel	uniform	133 mpy	simulated white water	4000 ppm				amb	8.6		16
	mild steel	uniform	33 mpy	simulated white water	4000 ppm				amb	11.6		16
	mild steel	uniform	25 mpy	simulated white water	4000 ppm				amb	13		16
	304 SS	pitting	N/A	simulated white water	3%	30%			115 F	5	3252.8 mohm/cm	16
	304 SS	pitting	N/A	simulated white water	6%	30%			115 F	5	3445.1 mohm/cm	16
	304 SS	pitting	N/A	simulated white water	10%	30%			115 F	5	3849.8 mohm/cm	16
	304 SS	pitting	N/A	simulated white water	15%	30%			115 F	5	4378.4 mohm/cm	16
	304 SS	pitting	N/A	simulated white water	30%	30%			115 F	5	7222.4 mohm/cm	16
	304 SS	pitting	N/A	simulated white water	20%	40%			115 F	5	7961.3 mohm/cm	16
	316 SS	pitting	N/A	simulated white water	3%	30%			115 F	5	3252.8 mohm/cm	16
	316 SS	pitting	N/A	simulated white water	6%	30%			115 F	5	3445.1 mohm/cm	16
	316 SS	pitting	N/A	simulated white water	10%	30%			115 F	5	3849.8 mohm/cm	16
	316 SS	pitting	N/A	simulated white water	15%	30%			115 F	5	4378.4 mohm/cm	16
	316 SS	pitting	N/A	simulated white water	30%	30%			115 F	5	7222.4 mohm/cm	16
	316 SS	pitting	N/A	simulated white water	20%	40%			115 F	5	7961.3 mohm/cm	16
	304 SS	deposit	N/A	simulated white water	3%	30%			115 F	5	3252.8 mohm/cm	16
	304 SS	deposit	N/A	simulated white water	6%	30%			115 F	5	3445.1 mohm/cm	16
	304 SS	deposit	N/A	simulated white water	10%	30%			115 F	5	3849.8 mohm/cm	16
	304 SS	deposit	N/A	simulated white water	15%	30%			115 F	5	4378.4 mohm/cm	16
	304 SS	deposit	N/A	simulated white water	30%	30%			115 F	5	7222.4 mohm/cm	16
	304 SS	deposit	N/A	simulated white water	20%	40%			115 F	5	7961.3 mohm/cm	16
	316 SS	deposit	N/A	simulated white water	3%	30%			115 F	5	3252.8 mohm/cm	16
	316 SS	deposit	N/A	simulated white water	6%	30%			115 F	5	3445.1 mohm/cm	16
	316 SS	deposit	N/A	simulated white water	10%	30%			115 F	5	3849.8 mohm/cm	16
	316 SS	deposit	N/A	simulated white water	15%	30%			115 F	5	4378.4 mohm/cm	16
	316 SS	deposit	N/A	simulated white water	30%	30%			115 F	5	7222.4 mohm/cm	16
	316 SS	deposit	N/A	simulated white water	20%	40%			115 F	5	7961.3 mohm/cm	16
Blend chest	1N bronze	pitting	severe"	real white water	373 mg/L	350 mg/L	0	11 mg/L	33 C	6.2	230 mS/m	21

Tray water	1N bronze	pitting	severe"	real white water	269-346 mg/L	430-541 mg/L	0	16 mg/L	42 C	4.0-4.4	180-220 mS/m	21
Uhle box	1N bronze	pitting	severe"	real white water	215-222 mg/L	344-348 mg/L	0	11 mg/L	35 C	4.2-4.5	120-130 mS/m	21
Head box	1N bronze	pitting	severe"	real white water	37-45 mg/L	334 mg/L	19-23 mg/L		44-47 C	5	240 mS/m	21
white water	1N bronze	pitting	severe"	real white water	37-40 mg/L	327 mg/L	20-21 mg/L		40-44 C	5	200-220 mS/m	21
Head box	1N bronze	pitting	severe"	real white water	77 mg/L	131 mg/L	32 mg/L	22 mg/L	52	6	300 mS/m	21
white water	1N bronze	pitting	severe"	real white water	79 mg/L	136 mg/L	28 mg/L	23 mg/L	48 C	6.3	260 mS/m	21
Tray water	1N bronze	pitting	severe"	real white water	78 mg/L	178 mg/L	32 mg/L	22 mg/L	49 C	6	300 mS/m	21
Head box	1N bronze	pitting	severe"	real white water	306 mg/L	4077 mg/L	0	203 mg/L	25 C	4.7	570 mS/m	21
Suction roll	1N bronze	pitting	severe"	real white water	285 mg/L	3655 mg/L	0	199 mg/L	25 C	4.7	570 mS/m	21

References on White Water Closure and its Effects on Equipment Corrosion

1. Adams, J. C., Valentine, G. E ., and Wyvill, J. C.;Mills Often Overlook Significant Water Recycling Opportunities, *Pulp Paper 60,* no. 4: 148-151 (April 1986).
2. Adams, J. C.., and Valentine, G. E, Wyvill, J. C.; Recycle Approaches for Paper and Pulp Mills, *Waterworld News* 1, no. 5: 18-20 (Sept./Oct. 1985).
3. Anderson, R., and Myhrman, R ., Closing of White Water System and Internal Cleaning of Effluents in Paper Mills, Int. Sem. Mgmt. Envir. *Problems Pulp Paper Ind.* (New Delhi): 263-274 (Feb. 24-25, 1982).
4. Askew, A. A.; Mill Water Close-up Problems and Specialty Chemical Answers, *Southern Pulp Paper Mfr*. 42, no. 4: 20-22 (April 1979).
5. Baker, J. R. and D. Howard; Reducing Mill Effluent and Dealing With the Consequences, *1995 Papermakers Conf.*, pp. 341-344. TAPPI Press, 1995.
6. Barton, A.B., Stuart, P.R., Lagace, P., Miner,R.; Experience with water system closure at recycled paperboard mills, *TAPPI J.*, Vol. 79, No. 3, 1996.
7. Bassidi, M. A. , Masounaue, J., Dickson, J. I.; A study of the effect of white water on fatigue in some stainless steels, pp108-112, *Pulp and Paper Industry Corrosion Problems*, Vol. 7, November 1992, Orlando, FL, TAPPI Press, 1992.
8. Bennett and C. J. Federowicz, Prediction of Localized Corrosion of Stainless Steels in White Water, *Materials Performance*, Vol. 21, No. 4, p. 39, 1982.
9. Bennett, C ; Control of Microbial Problems and Corrosion in Closed Systems, *Paper Technol. Ind.* 26, no. 7: 331-335 (Nov. 1985).
10. Bennett, D. C.; Introduction to Electrochemical Techniques for Investigating the Effects of Paper Mill or Bleach Plant Closure on the Corrosion Performance of Stainless Steels, *TAPPI Envir. Conf.* (Mobile) Proc.: 309-313 (April 22-24, 1985).
11. Bianchin, B., Gervason, G., and Vallette, P ;Closure of Circuits - Problems - Laboratory Simulation Test, *ATIP Rev.* 33, no. 9: 442-453, 429 (Nov. 1979).
12. Bihani, B. G.; Goal of Closed-Cycle Operation Hinges on Fiber-Line Developments, *Pulp Pap.* 70, no. 7: 87-90 (July 1996).
13. Bolton, System Approach To Reusing White Water On Paper Machines, *1995 Papermakers Conf.*, pp. 363-366. TAPPI Press, 1995.
14. Bowers, D. F.;Changes in Water Properties and Corrosivity with Closure, *Tappi J.*, Vol. 66, No. 9, p. 68, 1989.
15. Bowers, D. F .; Corrosion Engineerong and Material Selection for Closed Systems, *TAPPI Envir. Conf.* (Denver) Proc.: 13-14 (April 8-11, 1980).
16. Bowers, D. F. ; Corrosion in Closed White Water Systems, *Tappi J.*, vol. 61, No. 3, March 1978.
17. Bowers, D. F.; Changes in Water Properties and Corrosivity with Closure, *TAPPI Envir. Conf.* (Atlanta) Proc.: 95-97 (March 2-4, 1983).
18. Bowers, D. F.; Corrosion Engineering Considerations for Energy-Saving Systems in the Paper Mill, *IPC NE Regional Conf. Energy Efficiency*: 65-68 (March 27, 1980).
19. Bowers, D. F.; Corrosion in Paper Machine Systems, *TAPPI Envir. Conf.* (Mobile) Proc.: 315-325 (April 22-24, 1985).
20. Bush, S. W ; Closed Mill Concept, *TAPPI Papermakers Conf. Proc.* (Atlanta): 121-124 (April 10-12, 1978).
21. Michel, G. M . , and Castillo, A. P.,; White-Water Evaluation Designed to Support Proper Suction-Roll Shell-Material Selection and Reduce, *TAPPI Eng. Conf. (Atlanta) Proc.* (Book 1): 19-31 (Sept. 11-14, 1989).
22. Corrosion in Closed Mills, *World Pap.* 220, no. 8: 30 (September 1995).
23. Dahl, C. B. and Neubauer, E. P; Modern Practices can Present Hazards to Stainless Steel Suction Rolls, *Paper Trade J.* 155, no. 34: 46, 48, 50 (Aug. 23, 1971).
24. Garner, A ., and Thompson, C. B.; Paper-Machine Corrosion and Progressive Closure of the White-Water System, *Proceedings [of the] 8th International Symposium and EFC [European Federation of*

Corrosion] Event No. 204 on Corrosion in the Pulp & Paper Industry, Stockholm, Sweden, May 16-19, 1995
25. Geller, A., and Gottsching, L .;Closing Water Systems Completely in the Federal Republic of Germany, *Tappi J.* 65, no. 9: 97-101 (Sept. 1982).
26. Geller, A.;Complete Water System Closure in Paper Mills -Experience in the Federal Republic of Germany, *PIRA Econ. Poll. Control Proc.* SPB/3: 30 p. (April 1, 1982).
27. Gorelov and A. K. Talybly, Corrosion Protection of the Equipment in Closed and Reduced Water Recycling Systems, *Pulp and Paper Industry Corrosion Problems*, Vol. 4, Swedish Corrosion Institute, pp.113, 1983.
28. Gudlauski, D. G.; Effluent Closure; White-Water System Closure Means Managing Microbiological Buildup, *Pulp Pap.* 70, no. 3: 161-162, 165 (March 1996)
29. Guest, D. A ., and Moore, G. K., Closing-up of Water Systems - Benefits and Effects, BPBIF Tech. Sect. *Conf. on Savings from Services: Energy & Water* (Edinburgh) 121st: 19 p. (Oct. 21-22, 1981).
30. Guest, D. A., and Moore, G. K.., Closing Up of Water Systems: Benefits and Effects, *Paper Technol. Ind.* 23, no. 2: 65-70 (March 1982).
31. Guillet, F., Muratore, E., Muratore, E., Pichon, M., and Rameau, J. J.; Corrosion Monitoring and Control in Paper Mills: Closed Water Systems and Condensate Networks, *Pulp Pap. Ind. Corrosion Problems/Int. Symp. Corrosion in Pulp & Paper Ind.* (Helsinki) 6th, Book B: 361-372 (Aug. 29-Sept. 1, 1989).
32. Hall, W. B., Koelling, H. A., and Lightsey, G. R.; .Evaluation of Corrosion in Pulp- and Paper-Mill White Water Reuse Applications, *U.S. Dept. Interior, Bur. Reclamation Tech. Completion Rept.* OWRT/RU-82/16: 32 p. (Oct. 1982).
33. Hall, W. B., Koeller, H. A ., Lightsey, G. R., Singletary, G. D.;Operational Problems Resulting from Increased Paper Mill White Water Reuse: Corrosivity and Foaming, *Proc. Water Reuse Symp.* (Washington, DC) 2nd (Water Reuse in Future) Vol. 1: 604-615 (Aug. 23-28, 1981).
34. Inoue, N ., Johnson, K. A., and Seo, Y.; New Designs (and) New Alloys Keep KUBOTA (LTD., JAPAN) PM (Paper-Machine) Suction Roll Shells Ahead of Toughened Running Conditions; *Paper Age* 15, no. 11: 26-27 (Nov. 1979).
35. Kurkela, N. Suutala, and J. Kemppainen, On the Slection of Stainless Steels in Bleach Plants and White Water Systems, *Pulp and Paper Industry Corrosion Problems,* Vol. 5, Canadian Pulp and Paper Association, pp.127, 1986.
36. Marshall, D. W., and Springer, A. M..; Progress with Water Recycling in Non-Integrated Fine-Paper and Board Manufacturing Operations, *Proc. AIChE/EPA Natl. Conf. Complete Water Reuse* (Chicago) 2d: 1155-1163 (May 4-8, 1975; publ. 1976).
37. Mueller and J. M. Muhonen, Pitting Corrosion of Stainless Steels in Six Paper machine Headboxes: Mechanism and Prevention, *Tappi J.*, Vol 55, No. 4, p. 589, 1972.
38. Muhonen, Corrosion of Stainless Steels in Whitewater, *Pulp and Paper Industry Corrosion Problems,* Vol. 1, NACE, pp.75, 1974.
39. Panchapakesan, B.;Closed White Water System Design, *1993 Papermakers Conf.*, pp. 219-225. TAPPI Press, 1993.
40. Paper Chemistry Round Table I: Toward Zero Discharge, *PIMA* 74, no. 10: 30, 32-37 (Oct. 1992).
41. Pietschker, The 100% Closed Water System - What To Expect, *1996 Papermakers Conf.*, pp. 521-528. TAPPI Press, 1996
42. Pryke, D. C., Reeve, D. W., and Tran, H. N ; Corrosion in the Closed-Cycle Mill, *Pulp & Paper Ind. Corrosion Problems/Proc. Int. Symp. Corrosion in Pulp & Paper Ind.* (Stockholm) 4th: 85-90 (May 30-June 2, 1983).
43. Reeser, D. M .; Survey Regarding the Reuse of Water or the Restriction of Fresh Water Flow for Paper-Machine Vacuum-Seal Water Pumps, *TAPPI Envir. Conf.* (Charleston) Proc.: 141-147 (April 18-20, 1988).
44. Robertson, L. R.; Paper Chemistry; Clean Machine with Minimal Fresh Water, *PIMA* 77, no. 4: 42-43 (April 1995).
45. Robertson, L. R.; Impact of water reuse on Microbial Colonization of Paper Machines, *1995 Papermakers Conf.*, pp. 351-362. TAPPI Press, 1995.
46. Safade, T. L.; Tackling the Slime Problem in a Paper Mill, *Paper Technol. Ind.* 29, no. 6: 280-285 (Sept. 1988

47. Sunds, G., and S. Strom, The Consequences of System Closure for Corrosion in Swedish Pulp and Paper Mills, *Pulp and Paper Industry Corrosion Problems*, Vol. 5, Canadian Pulp and Paper Association, pp.51, 1986.
48. Thompson, C. B., and A. Garner; Paper Machine Corrosion and Progressive Closure of The White Water System, *1996 Papermakers Conf.*, pp. 545-552. TAPPI Press, 1996.
49. Thorpe, P. H .; Microbiological Corrosion of Stainless Steel in Paper Machines and its Causes, *Pulp & Paper Ind. Corrosion Problems/Int. Symp. Corrosion in Pulp & Paper Ind.* (Vancouver) 5th: 169-173 (June 3-6, 1986).
50. Thorpe, P. H. ;Corrosion Control in Paper Machines, *Appita*, Vol. 35, No. 6, pp. 505-511, 1982
51. Thorpe, P. H.; Corrosion in Paper Machines - An Overview, *Pulp and Paper Industry Corrosion Problems,* Vol. 3, pp. 184-, NACE , 1980.
52. Wensley, Localized Corrosion Resistance of Stainless Steels in White Waters, *Materials Performance*, Vol. 28, No. 11, p 68, 1989.
53. Wenzl, D. J. H .; Closure of Paper and Board Mill Production Systems and its Effects on Production Conditions, *TAPPI Ann. Mtg.* (Chicago) Proc.: 95-109 (March 2-5, 1981).

(Publications in Languages other Than English)

54. Arestova, G. A., Litvinova, S. T., Mil'shtein, A. D ., and Svitel'skii, V. P.; Principles for Design of Water Consumption Systems at Board Mills, *Bumazh. Prom.* no. 6: 9-12 (June 1980).
55. Arestova, G. A.., Kovba, V. A ., Litvinova, S. T., and Svitel'skii, V. P., Circulating Water System at Pulp and Paper Mills-Important Part of Low-Waste and Wasteless Technology, *Sb. Nauch. Tr. UkrNPOBumProm.*, Prob. Oblasti Okhrany Okruzh. Sredy Tsellyul.-Bumazh. Prom. (Gritsulyak, V. N., ed.): 14-20 (1982 Kiev). [Russ.]
56. Baumgarten, H. L., Geller, A. N., and Sangl, R. G.; Optimizing Water Economy in Paper Mills, *Pulp and Paper 2000*, Vol. 2: 213-247 (Oct. 8, 1993).[Ger.; Engl. & Fr. sum.]
57. Borner, F,.,Brecht, and W., Dalpke, H.-L.;Closed Water Circulation Systems in Additional Paper Mills Processing Waste Paper, *Wochbl. apierfabr.* 102, no. 7: 223-34 (April 15, 1974).
58. Borner, F., Dalpke, H.-L., Geller, A., and Gottsching, L ;Enrichment of Salts in Process Water and Paper by Closing Water Circuits in Paper Mills. (1). Theoretical Basis and Practical Experience with Closed Circuits, *Wochbl. Papierfabr.* 110, no. 9: 287-288, 290-292, 294, (May 15, 1982).
59. Bottcher, H.., Breuer, H., Dalpke, H.-L., Gissler-Weber, R.., and Minne, S ; Solution of Problems with a Closed Circuit for Process Water in a Paper Mill Using Waste Paper, Wochbl. *Papierfabr.* 109, no. 21: 797-798, 800-802, 804-805 (Nov. 15, 1981).
60. Demel, I., and Mobius, C. H .; Corrosion in Paper Mills, *Allg. Papier-Rundschau* no. 24/25: 746, 748, 750, 752, 754-755 (June 19, 1987).
61. Demel,I., and Mobius, C. H.; Corrosion in Paper Mills, Alleg. Papier-Rundscheu, No. 24/25: 746 (June 19, 1987). [Ger.]
62. Environmental Conditions Increase Corrosion Problems, *APR Allg. Pap.-Rundsch.* 119, no. 20: 514-515 (May 20, 1995).
63. Fredang, B., and Geldmacher, J.; Optimization of Water Circuits in Paper Mills by Using Disk Filters as a Separator System, *Allg. Pap.-Rundsch.* no. 40: 1087-1088, 1090-1091 (Oct. 5, 1990). [Ger.]
64. Gorelov, V. V., Grigor'eva, N. K., Podosenova, T. N., and Talybly, A. K.Microbiological Corrosion of Equipment in Closed-Circuit Paper and Board Mills, *Sb. Tr. VNIIB*, chistka Stochn. Vod Utiliz. Osadkov Tsellyul.-Bumazh. Prom.: 37-50 (1988 Leningrad). [Russ.]
65. Gorelov, V. V., Mordventsev, V. V., Oshchphovo, M. V., and Sergev,S. G.; Protection of Instalattions from Corrosion in a Closed Water Supply System, *Sb. Tr. VNIIB*, chistka Stochn. Vod Utiliz. Osadkov Tsellyul.-Bumazh. Prom.: 29-36 (1988 Leningrad). [Russ.]
66. Hurst-Gaul, E .; Closure of the Water Circuit in Fine-Paper Mills, *Serial analytic*, 1979
67. Kuron, D., and Rother, H.-J ., Protection Against Corrosion by Inhibitors, *Wochbl. Papierfabr.* 109, no. 19: 717-718, 720-724, (Oct. 15, 1981). Flemming, H.-C., Klare, J. Lustenberger, M.; Microbiological Problems in the Paper Industry; Damage, causes, Costs, Fundamentals, *Papier* 50, no. 2: 47-53 (February 1996). [Ger.; Engl. sum.]
68. Muratore, E., Pichon, M., and Rameau, J. J ; Closed [White Water] Systems and Corrosion in a Paper Mill, *ATIP Rev.* 40, no. 1: 2, 21-29 (Jan. 1986). [Fr.; Engl. sum.]

69. Springer, A. M .; Considerations in Process Water Reuse in Non-Integrated Mill [Engl.; Finn. sum.]
70. Sund, G .; Corrosion Problems in the Closed Pulp and Paper Mill -Survey, *korrosionsinstitutet KI Rappt.* 1984/3: 36 p. (Aug. 2, 1984). [Swed.; Engl. sum.] [Avail. from Swed. Corrosion, Inst., Box 5607, 114-86 Stockholm